Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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Alan R. Katritzky[a]; James W. Rogers[a]; Rachel M. Witek[a]; Anatoliy V. Vakulenko[a]; Prabhu P. Mohapatra[a]; Peter J. Steel[b]; Reddy Damavarapu[c]
[a] Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida [b] Department of Chemistry, University of Canterbury, Christchurch, New Zealand [c] U.S. Army ARDEC, Picatinny Arsenal, New Jersey

To cite this Article Katritzky, Alan R. , Rogers, James W. , Witek, Rachel M. , Vakulenko, Anatoliy V. , Mohapatra, Prabhu P. , Steel, Peter J. and Damavarapu, Reddy(2007) 'Synthesis and Characterization of Blowing Agents and Hypergolics', Journal of Energetic Materials, 25: 2, 79 — 109
To link to this Article: DOI: 10.1080/07370650701204702
URL: http://dx.doi.org/10.1080/07370650701204702

Journal of Energetic Materials, 25: 79–109, 2007

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650701204702

Synthesis and Characterization of Blowing Agents and Hypergolics

ALAN R. KATRITZKY
JAMES W. ROGERS
RACHEL M. WITEK
ANATOLIY V. VAKULENKO
PRABHU P. MOHAPATRA

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida

PETER J. STEEL

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

REDDY DAMAVARAPU

U.S. Army ARDEC, Picatinny Arsenal, New Jersey

Twelve energetic additives ***7–18*** *were synthesized and evaluated for use as blowing agents. All blowing agent candidates were characterized by NMR spectroscopy, elemental analysis, differential scanning calorimetry, thermogravimetric analysis, and impact sensitivity testing. The X-ray crystal structure of pyrazolium nitrate was also determined. Hypergolic compounds imidazolidine* ***38a****, hexahydropyrimidine* ***38b****, and pyrrolidine derivatives* ***42*** *were obtained in improved 80–90% yields by the reduction of the corresponding carbonyl compounds with lithium aluminum hydride in ether under reflux for 12 h.*

Address correspondence to Alan R. Katritzky, Department of Chemistry, University of Florida, 127 Chemistry Research Bldg, Gainesville, FL 32611. E-mail: katritzky@chem.ufl.edu

Ignition delays (τ_{exp}, μs) were determined for compounds ***38a,b*** *and* ***42****.*

Keywords: blowing agents, characterization, hypergolic compounds, synthesis

Introduction

The rubber industry employs blowing agents (gas-generating agents) such as dinitropentamethylenetetramine and *p*-tolylsulfonylhydrazide in the production of microcellular rubber [1]. Azodicarbonamide (**1**), Exocerol 232 (**2**), and Hydrocerol BIH (**3**) are blowing agents that are now commonly used in the plastics industry and replace CFCs previously used to provide polymer foams (Fig. 1) [2–4]. Another significant application of blowing agents is their use in propellant formulations [5,6]. During the past two decades, a large number of blowing agents based on organic azides have been synthesized and successfully examined as ingredients for propellants or plastic-bonded explosives [7].

Many nitro-substituted heterocycles are valuable as energetic additives for use in propellants and explosives [8]. In

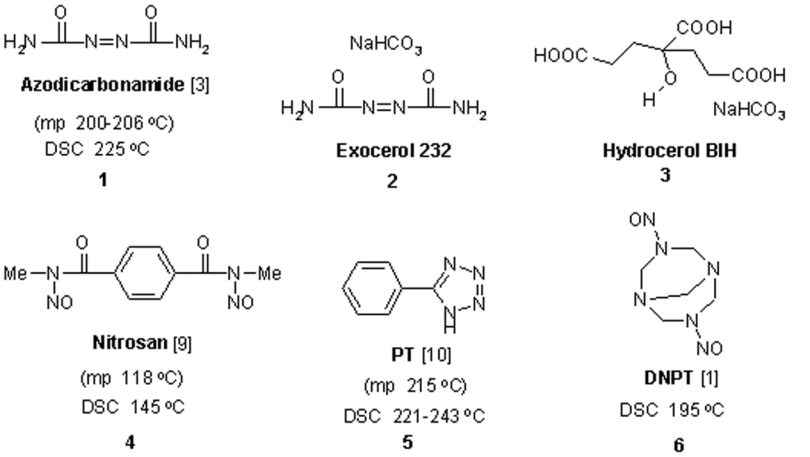


Figure 1. Commercially available blowing agents **1**–**6**.

previous studies on the nitration of heterocycles [12], we reported convenient access to polynitroimidazole [13], trinitroazetidine [14], nitropyridines [15], and mononitro five-membered heterocycles [16]. Recently we have synthesized an ionic liquid containing an energetic anion [17]. In a collaborative effort with the U.S. Army to develop novel munitions formulations, we have investigated the synthesis and characterization of energetic compounds that could provide new blowing agents. The U.S. Army has previously applied blowing agents (e.g., 2,4-dinitrophenylhydrazine) as energetic material additives in explosive mixtures to modify general munitions properties. Inclusion of blowing agents that display separate isotherms from the other components of explosive mixtures is a means of tempering the violence of explosions. For a particular army formulation containing trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), inclusion of blowing agents possessing a DSC of $\sim$180°C provides a means of bursting open any confinement before reaction of the main constituents, thus mitigating cook-off violence.

Of particular interest are blowing agents with the following characteristics: quick generation of gas, mp higher than 75°C, and storage stability and with DSC that indicates gas evolution at 140–200°C. Commercially available stable blowing agents **1**–**6** (utilized in the plastics and rubber industry) are reported to possess suitably high melting points and suitable DSCs (Fig. 1) [3, 9–11, 18]. We tested 16 compounds: 4 were commercially available (**1**, **4**–**6**) and the other 12 were synthesized (Fig. 2): pentaerythritol tetranitrate (PETN)(**7**), heterocyclic nitrate salts (**8**–**10**), and derivatives (**11**–**18**). The literature reports syntheses of other energetic additives **11**–**14**, **16**, and **17** that possess measurable melting points but do not have recorded DSC values (Fig. 2). To obtain DSC data for the evaluation of the suitability of energetic additives **11**–**18** as blowing agents, we developed reasonable syntheses that can potentially be scaled up to provide 50–100 g quantities of these compounds. Additionally, we have taken thermogravimetric analyses (Tg_a) of compounds **11**–**18** to provide supplementary data for comparison with DSC analyses.

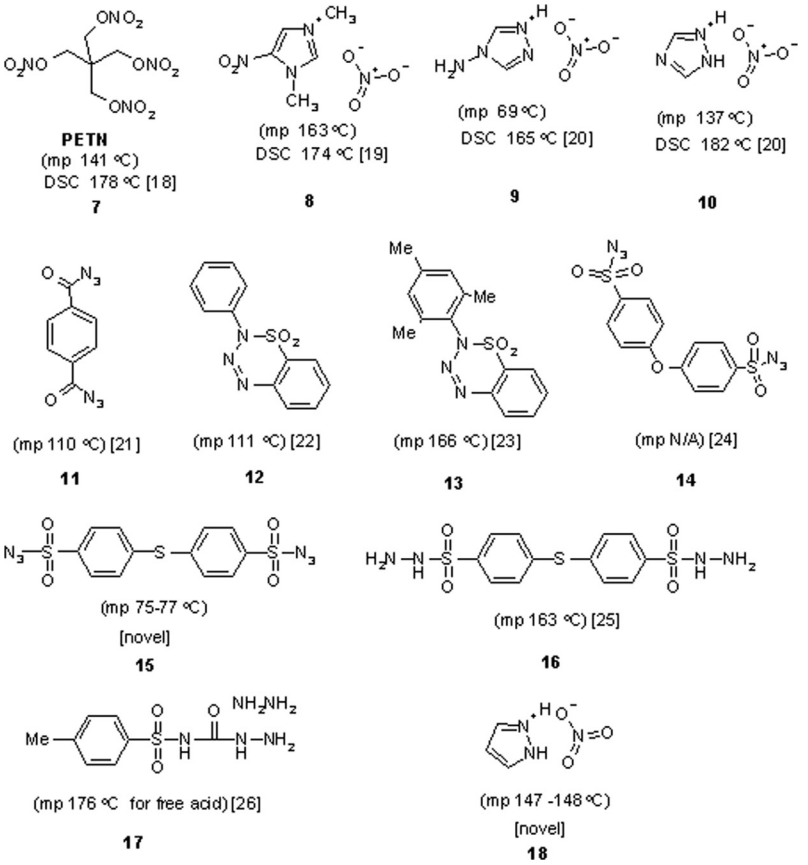


Figure 2. Energetic additives **7**–**18**.

Hypergolic compounds as well as blowing agents are used in propellant formulations [27]. Basically, hypergolic propellants are rocket fuels and oxidizers, which ignite spontaneously on contact with each other and require no ignition source. The easy start and restart capability of hypergolics make them ideal for spacecraft maneuvering systems. Hypergolic fuels commonly include hydrazine, monomethyl hydrazine (MMH), and unsymmetrical dimethyl hydrazine (UDMH). Hydrazine gives the best performance as a rocket fuel, but it has a high freezing point and is too unstable for use as a coolant. Additionally,

most current hypergolic compounds are highly toxic, carcinogenic, and explosive [28]. These problems have prompted the additional search for new types of hypergolic candidates based on nitrogen containing five- and six-membered heterocycles.

Experimental

Caution! Although we have not experienced any problems in synthesizing or handling them, these materials should be treated with extreme care and all appropriate safety precautions followed.

General Methods

Melting points were determined using a Bristoline hot-stage microscope and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a 300-MHz NMR spectrometer in DMSO-d_6 or chloroform-d solution as indicated. THF was distilled from sodium-benzophenone ketal prior to use. Column chromatography was performed on silica gel (300–400 mesh). Elemental analyses were performed on a Carlo Erba-1106 instrument. For the DSC and TGA experiments, instruments (2960 SDT V3.OF) Perkin-Elmer DSC 7 or Perkin-Elmer TGA 7 were used to analyze samples (∼3 mg) with heating rates of 10 or 20°C/min in open aluminum pans in an argon atmosphere with flow rate equal to 50 mL/min. Thermal calibrations for differential scanning calorimetry were made using indium and freshly distilled *n*-octane as references. Heats of fusion were referenced against indium. TG/DTA analyses for compounds **8**, **14**–**17** were performed on a Seiko TG/DTA 320 instrument with a heating rate of 10°C/min in an argon atmosphere with flow rate equal to 50 mL/min. Ignition delays (τ_{exp}, μs) were measured by high-speed photography of mixing of amine with inhibited red fuming nitric acid on an apparatus reported by Slocum-Wang et al. [29].

Materials

Pentaerythritol tetranitrate (**7**) [30] and 2-amino-*N*-arylbenzenesulfonamides (**28**) [22] were synthesized according to the slightly

modified published procedure. Pentaerythritol, 5-nitroimidazole, 4-amino-1,2,4-triazole, 1,2,4-triazole, terephthaloyl chloride, diphenyl ether, diphenyl sulfide, 4-tolylsulfonyl isocyanate, and pyrazole were purchased and used without further purification.

Synthesis of Blowing Reagent Candidates **7**–**18**

Pentaerythritol tetranitrate, **7** Pentaerythritol (4.80 g, 0.015 mol) and urea (0.03 g) were added at 0°C to 19.80 g of 90% concentrated nitric acid. Stirring was continued for 15 min, then 96% concentrated sulfuric acid (19.80 g) was added, and the reaction mixture was left to stir at 0°C for 2 h. The whole was poured onto ice, filtered, and washed with water (400 mL). The precipitate was dissolved in 250 mL of acetone containing 0.75 g of ammonium carbonate by heating in a water bath at 50°C. Ethanol (72 mL) and water (108 mL) were then added. Pentaerythritol tetranitrate (**7**) crystallized out over 2 h. Filtration and washing the precipitate with ethanol afforded a near quantitative yield (99%) of pentaerythritol tetranitrate (**7**) as white needles, mp 140°C (Lit. [30] mp 141°C).

^{1}H NMR (Acetone-d_6/DMSO-d_6,) δ ppm: 4.77 (s, 8H); ^{13}C NMR (Acetone-d_6/DMSO-d_6,) δ ppm: 68.6 (4C), 41.0.

Elemental analysis: Theory: % C, 19.00; % H, 2.55; % N, 17.72. Found: % C, 19.29; % H, 2.44; % N, 17.35.

Heterocyclic Nitrate Salts **8**–**10**

1,3-Dimethyl-4-nitroimidazolium nitrate, **8** To a magnetically stirred solution of 1,3-dimethyl-4-nitroimidazolium iodide **22** [19] (0.94 g) in water (30 mL) was added silver nitrate (0.59 g). After 2 h at room temperature, silver iodide was removed by filtration. The filtrate was dried in vacuo at 60°C to give **8** as colorless needles in 98% yield, mp 162.0–163.0°C (Lit. [19] mp 163°C).

^{1}H NMR (CD_3OD) δ ppm: 9.18 (s, 1H), 8.74 (s, 1H), 4.28 (s, 3H), 4.12 (s, 3H); ^{13}C NMR (CD_3OD) δ ppm: 139.3, 137.5, 125.3, 36.8, 36.8.

Elemental analysis: Theory: % C, 29.42; % H, 3.95; % N, 27.45. Found: % C, 29.53; % H, 3.88; % N, 27.05.

4-Amino-1,2,4-triazolium nitrate, **9** Concentrated nitric acid (0.75 g, 8.1 mmol) was added dropwise to a solution of 4-amino-1,2,4-triazole **23** (0.68 g, 8.1 mmol) in dry methanol (9 mL) under nitrogen flow at room temperature. The colorless, homogeneous reaction mixture was stirred for 1 h at ambient temperature. At the end of one hour, the stir bar was removed and solvent was evacuated under high vacuum overnight to give **9** as colorless prisms in 89% yield, mp 67.0–68.0°C (Lit. [20] mp 69°C).
^{1}H NMR (CD_3OD) δ ppm: 9.35 (s, 2H), 5.04 (s, 3H); ^{13}C NMR (CD_3OD) δ ppm: 145.8.

Elemental analysis: Theory: % C, 16.33; % H, 3.43; % N, 47.61. Found: % C, 16.72; % H, 3.25; % N, 47.38.

1,2,4-Triazolium nitrate, **10** Concentrated nitric acid (0.77 g, 8.3 mmol) was added dropwise to a solution of 1,2,4-triazole **24** (0.57 g, 8.3 mmol) in dry methanol (9 mL) under nitrogen flow at room temperature. The colorless, homogenous reaction mixture was stirred for 1 h at ambient temperature. At the end of one hour, the stir bar was removed and solvent was evacuated under a high vacuum overnight to give **10** as white microcrystals in 93% yield, mp 137.0–138.0°C (Lit. [20] mp 137.0°C).
^{1}H NMR (CD_3OD) δ ppm: 9.30 (s, 1H); 5.25 (s, 1H); ^{13}C NMR (CD_3OD) δ ppm: 143.9.

Elemental analysis: Theory: % C, 18.19; % H, 3.05; % N, 42.42. Found: % C, 18.57; % H, 2.90; % N, 42.05.

Azido[4-(azidocarbonyl)phenyl]methanone, **11** To a cooled solution of sodium azide (0.15 g, 2.3 mmol) in water (15 mL) was added dropwise an ice-chilled solution of terephthaloyl chloride (**25**) (0.203 g, 1 mmol) in acetone (10 mL). After addition was complete, water (5 mL) was added and the reaction mixture was stirred at rt for an additional 30 min. The precipitate was filtered off, washed with water, and dried under vacuum to give **11** as white microcrystals in 83% yield, mp 105–106°C (Lit. [21] mp 110°C).

^{1}H NMR (DMSO-d_6) δ ppm: 8.09 (s, 4H); ^{13}C NMR (DMSO-d_6) δ ppm: 171.5, 135.2, 129.5.

Elemental analysis: Theory: % C, 44.45; % H, 1.87; % N, 38.88. Found: % C, 44.69; % H, 1.67; % N, 38.60.

2-Substituted Benzo[1,2,3,4]Thiatriazine-1,1-Dioxides **12–13**

2-Phenyl-2H-benzo[1,2,3,4]thiatriazine 1,1-dioxide, **12** Sodium nitrite (0.36 g, 5.2 mmol) was added to a stirred solution of 2-amino-*N*-phenylbenzenesulfonamide (**28a**) [22] (1.0 g, 3.5 mmol) dissolved by gentle warming in aqueous 95% acetic acid (50 mL) and then cooled to 25°C. The resulting mixture was stirred at 25°C for 8 h, then ice-cold water (200 mL) was added and the precipitated product was filtered and washed with water. The red solid was dried in vacuo overnight to afford a 75% yield of 2-phenyl-2*H*-benzo[1,2,3,4]thiatriazine 1,1-dioxide **12** as red microcrystals, mp 110–111°C (Lit. [22] mp 111°C).

2-(2,4,6-Trimethylphenyl)-2H-benzo[1,2,3,4]thiatriazine 1,1-dioxide, **13** Sodium nitrite (0.32 g, 4.6 mmol) was added to a stirred solution of 2-amino-*N*-(2,4,6-trimethylphenyl)-benzenesulfonamide (**28b**) [23] (1.0 g, 3.1 mmol) dissolved by gentle warming in aqueous acetic acid 95% (50 mL) and then cooled to 25°C. The resulting mixture was stirred at 25°C for 8 h, then ice-cold water (200 mL) was added and the precipitated product was filtered and washed with water. The red solid was dried in vacuo overnight to afford a 74% yield of 2-(2,4,6-trimethylphenyl)-2*H*-benzo[1,2,3,4]thiatriazine 1,1-dioxide **13** as red microcrystals, mp 163–165°C (Lit. [23] mp 166°C).

Disulfonyl Dichloride Derivatives **14–16**

4-[4-(Chlorosulfonyl)phenoxy]benzenesulfonyl chloride, **30** In a round-bottom flask at room temperature, chlorosulfonic acid (20 mL) was slowly added to neat diphenyl ether (**29**) (8.5 g, 0.05 mol). (*Caution*: reaction very exothermic.) The reaction mixture was stirred at rt for 2 h. The mixture was then poured into ice water (200 mL), and the crude disulfonyl dichloride was collected by filtration and thoroughly washed

with water. Drying under vacuum gave **30** as an off-white powder in 74% yield, mp 126–127°C (Lit. [31] mp 128–129°C). ^{1}H NMR (DMSO-d_6) δ ppm: 8.10 (d, $J = 9.0$ Hz, 4H), 7.30 (d, $J = 9.0$ Hz, 4H); ^{13}C NMR (DMSO-d_6); δ ppm: 157.6, 138.3, 127.5, 118.0.

Elemental analysis: Theory: % C, 39.25; % H, 2.20; % N, 0.00. Found: % C, 38.88; % H, 2.06; % N, 0.01.

Bis[4-(azidosulfonyl)phenyl] ether, **14** [24] To disulfonyl dichloride **30** (0.37 g, 1 mmol) dissolved in acetone at 0°C was added sodium azide (0.16 g, 2.4 mmol). Stirring was continued for 18 h with the reaction mixture allowed to slowly warm to rt. Water (100 mL) was added and the precipitate filtered and recrystallized from acetone/water to give the desired sulfonyl azide **14** as colorless microcrystals in 83% yield, mp 84–86°C. ^{1}H NMR (DMSO-d_6) δ ppm: 8.01 (d, $J = 9.0$ Hz, 4H), 7.25 (d, $J = 9.0$ Hz, 4H); ^{13}C NMR (DMSO-d_6); δ ppm: 160.6, 134.2, 130.3, 119.9.

Elemental analysis: Theory: % C, 37.89; % H, 2.12; % N, 22.09. Found: % C, 38.00; % H, 1.95; % N, 21.90.

4,4′-Sulfanediyl-bis-benzenesulfonyl chloride, **32** In a round-bottom flask at room temperature, chlorosulfonic acid (4 mL, excess) was slowly added to neat diphenyl sulfide (**31**) (1.7 mL, 0.010 mol). (*Caution*: reaction very exothermic.) The reaction mixture was stirred at rt for 4 h and then poured into ice water (200 mL). The crude disulfonyl dichloride was collected by filtration and thoroughly washed with water. Drying under vacuum gave **32** as a white powder in 41% yield, mp 149–151°C (Lit. [25] mp 155–156°C). ^{1}H NMR (DMSO-d_6) δ ppm: 7.60 (d, $J = 8.1$ Hz, 4H), 7.28 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (DMSO-d_6) δ ppm: 147.2, 135.1, 130.0, 126.8.

Elemental analysis: Theory: % C, 37.60; % H, 2.10; % N, 0.00. Found: % C, 37.60; % H, 1.94; % N, 0.01.

4,4′-Thiobis-benzenesulfonyl azide, **15** To disulfonyl dichloride **32** (0.39 g, 1 mmol) dissolved in acetone at 0°C was

added sodium azide (0.16 g, 2.4 mmol). Stirring was continued for 18 h with the reaction mixture allowed to slowly warm to rt. Water (100 mL) was added and the precipitate filtered and recrystallized from acetone/water to give the desired sulfonyl azide **15** as colorless microcrystals in 18% yield, mp 75–77°C. ^{1}H NMR (DMSO-d_6) δ ppm: 7.93 (d, $J = 8.4$ Hz, 4H), 7.56 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (DMSO-d_6) δ ppm: 142.7, 137.7, 131.4, 128.5.

Elemental analysis: Theory: % C, 36.36; % H, 2.03; % N, 21.20. Found: % C, 36.47; % H, 1.84; % N, 20.90.

4,4′-Thiobis(benzenesulfonyl hydrazide), **16** The disulfonyl dichloride **32** (0.39 g, 1 mmol) was dissolved in ethanol at 0°C. Hydrazine (0.1 mL, 5 mmol, 5 equiv.) was added dropwise and the reaction was stirred at 0°C for 2 h. Then, ice water (50 mL) was added and the precipitate filtered to give crude product, which was recrystallized from ethanol, providing colorless microcrystals in 72% yield, mp 162°C (Lit. [25] mp 163°C). ^{1}H NMR (DMSO-d_6) δ ppm: 8.16 (s, 2H), 7.88 (d, $J = 8.7$ Hz, 4H), 7.48 (d, $J = 8.4$ Hz, 4H), 3.63 (br s, 4H); ^{13}C NMR (DMSO-d_6) δ ppm: 139.3, 136.9, 130.4, 128.7.

Elemental analysis: Theory: % C, 38.49; % H, 3.77; % N, 14.96. Found: % C, 38.47; % H, 3.73; % N, 14.57.

N-(Hydrazinocarbonyl)-4-Methylbenzenesulfonamide Hydrazine Salt **17**

N-Ethoxycarbonyl-(4-methylphenyl)sulfonamide, **34** 4-Tolylsulfonyl isocyanate **33** (2.6 g, 13.2 mmol) was slowly added to 25 mL of dry ethanol at −20°C. The reaction mixture was stirred at −20°C for 2 h then at rt for 18 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to provide *N*-ethoxycarbonyl-(4-methylphenyl)sulfonamide **34** in 92% yield as white cubes, mp82–84°C (Lit. [32] mp 82–84°C). ^{1}H NMR ($CDCl_3$) δ ppm: 7.93 (d, $J = 8.4$ Hz, 2H), 7.57 (br s, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 4.13 (q, $J = 7.8$ Hz, 2H), 2.45 (s, 3H), 1.21 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ ppm: 150.5, 145.0, 135.5, 129.6, 128.4, 63.1, 21.6, 14.0.

N-(Hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt, **17** A mixture of ethyl *N*-(4-toluenesulfonyl) carbamate **34** (1.22 g, 5 mmol), hydrazine hydrate (10 mmol) and absolute ethanol (50 mL) were refluxed on a steam bath for 8 h. On cooling, a solid was filtered and washed with ethanol to give *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide •($0.75N_2H_4$) **17** as white microcrystals in 84% yield, mp 136.0–139.0°C.

^{1}H NMR (DMSO-d_6) δ ppm: 7.65 (d, $J = 8.1$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.61 (br s, 4H), 2.31 (s, 3H); ^{13}C NMR (CD_3OD) δ ppm: 161.4, 143.4, 139.5, 128.2, 126.6, 20.9.

Elemental analysis: Theory for $C_8H_{11}N_3O_3S$•($0.75N_2H_4$): % C, 37.94; % H, 5.57; % N, 24.88.

Found: % C, 38.30; % H, 5.74; % N, 25.13.

Pyrazolium nitrate, **18** A Schlenk flask with pyrazole (**35**) (0.68 g, 10 mmol) was attached to a pump and dried under vacuum for 30 min. The flask was cooled in an ice bath and trifluoroacetic anhydride (TFAA) (6.5 mL) was added through the septum. Addition of 2.2 mL of 70% nitric acid was carried out after the addition of TFAA by very slowly adding 0.5–0.7 mL aliquots of nitric acid dropwise through the septum (dropwise with medium stir rate [500 rpm]) allowing 15 min of stirring between each addition. After complete addition of nitric acid, the reaction was left to stir at room temperature for 12 h. Solvent was removed under vacuum. Recrystallization of the crude product from ethyl acetate gave pyrazolium nitrate **18** as white needles in 65% yield, mp 147–148°C. Solvent was evaporated from the recrystallization filtrate and the residue was purified by silica gel column (eluent ethyl acetate/hexane = 2/1) to give 4-nitropyrazole **36** in 30% yield.

^{1}H NMR (DMSO-d_6) δ ppm: 15.14 (s, 2H), 8.26 (d, $J = 2.4$ Hz, 2H), and 6.71 (t, $J = 2.4$ Hz, 1H); ^{13}C NMR (DMSO-d_6) δ ppm: 133.9, 106.5.

Elemental analysis: Theory: % C, 27.49; % H, 3.84; % N, 32.05.

Found: % C, 27.88; % H, 3.72; % N, 31.68.

4-Nitropyrazole, **36** White microcrystals, 30% yield, mp 163.0–164.0°C (Lit. [33] mp 162.0–164.0°C).

^{1}H NMR (DMSO-d_6) δ ppm: 12.76 (br s, 1H), 8.59 (s, 2H); ^{13}C NMR (DMSO-d_6) δ ppm: 135.5, 132.4.

Synthesis of Hypergolic Candidates **38**, **42**

General procedure for reduction of cyclic carbonyl compounds **37**, **41** Lithium aluminum hydride (19.2 mmol) was suspended in anhydrous diethyl ether (160 mL). The corresponding cyclic carbonyl compound (16.8 mmol for **37** or 8.4 mmol for **41**) was added dropwise to the obtained suspension and the reaction mixture was refluxed gently for 12 h. Water (5 mL) and then a 2*N* solution of NaOH (2 mL) were added slowly at 0–5°C to quench the reaction. The solid was then filtered off and diethyl ether was removed under reduced pressure to afford cyclic tertiary amines **38**, **42**.

1,3-Dimethylimidazoline, **38a** Colorless oil, 80% yield, bp 109.0–111.0°C, (Lit. [34] bp 108.0–111.0°C). Ignition delay, τ_{exp}, μs: 45.
^{1}H NMR ($CDCl_3$) δ ppm: 3.15 (s, 2H), 2.63 (s, 4H), 2.25 (s, 6H); ^{13}C NMR ($CDCl_3$) δ ppm: 79.8, 54.3, 41.5.

1,3-Dimethylhexahydropyrimidine, **38b** Colorless oil, 95% yield, bp 110.0–115.0°C (Lit. [35] bp 110.0–115.0°C). Ignition delay, τ_{exp}, μs: 76.
^{1}H NMR ($CDCl_3$) δ ppm: 2.97 (br s, 2H), 2.40–2.43 (m, 4H), 2.24 (s, 6H), 1.67–1.72 (m, 2H,); ^{13}C NMR ($CDCl_3$) δ ppm: 79.6, 54.1, 43.1, 23.9.

N,N-Dimethyl-2-(1-pyrrolidinyl)-1-ethanamine, **42** Yellowish oil, 87% yield, bp 92.0–94.0°C/48 mm/Hg (Lit. [36] bp 92.0–94.0°C/48 mm/Hg). Ignition delay, τ_{exp}, μs: 71.
^{1}H NMR ($CDCl_3$) δ ppm: 2.47–2.54 (m, 6H), 2.35–2.40 (m, 2H), 2.19 (s, 6H), 1.70–1.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ ppm: 56.5, 52.34, 52.32, 43.9, 21.4.

1-(2-Dimethylamino-ethyl)-pyrrolidine-2,5-dione, **41** *N,N*-Dimethyl-ethane-1,2-diamine (5 mL, 71 mmol) was added to succinic anhydride (7.07 g, 71 mmol) with stirring and

the reaction mixture was heated with a microwave synthesizer (110°C, 100 W for 2 min and 150°C, 100 W for 5 min). The mixture was then distilled at reduced pressure to afford 1-(2-dimethylamino-ethyl)-pyrrolidine-2,5-dione **41** as a colorless oil in 59% yield, bp 94.0–96.0°C/2 mm/Hg (Lit. [36] bp 93.0–97.0°C/2 mm/Hg).
^{1}H NMR ($CDCl_3$) δ ppm: 3.42 (t, $J = 6.6$ Hz, 2H), 2.53 (s, 4H), 2.30 (t, $J = 6.6$ Hz, 2H), 2.06 (s, 6H); ^{13}C NMR ($CDCl_3$) δ ppm: 176.8, 55.6, 44.8, 36.0, 27.6.

X-Ray Crystallography

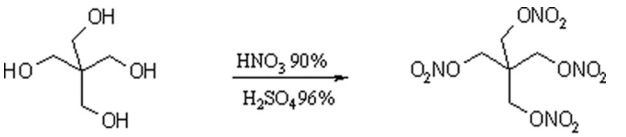
Intensity data for (**18**) were collected with a Siemens SMART CCD area detector using monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. A total of 3494 reflections were collected which, after merging ($R_{int} = 0.0389$), gave 937 unique reflections. The intensities were corrected for Lorentz and polarization effects and for absorption.

The structure was solved by direct methods using SHELXS [37] and refined on F^2 by full-matrix least-squares procedures using SHELXL97 [38]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The positions of hydrogen atoms were refined with isotropic displacement coefficients equal to 1.2 times the isotropic equivalent of their carrier atoms. A final difference map showed no features greater or less than 0.24 e–/Å^3.

Crystal data for (**18**): $C_3H_5N_3O_3$, MW 131.10, monoclinic, space group $P2_1/c$, $a = 3.697(3)$, $b = 11.221(11)$, $c = 13.195(12)$ Å, $\beta = 94.177(16)°$, V = 546.0(9) Å^3, F(000) = 272, Z = 4, T = −160°C, μ (MoKα) = 0.142 mm^{-1}, D_{calcd} = 1.595 g·cm^{-3}, $2\theta_{max}$ 50°, wR(F^2) = 0.0925 (all 937 data), R = 0.0385 (634 data with $I > 2\sigma I$).

Results and Discussion

Synthesis of PETN **7** Synthesis of PETN (**7**) was accomplished in near quantitative yield (99%) using excess fuming nitric (90%) and concentrated sulfuric acid (96%) in



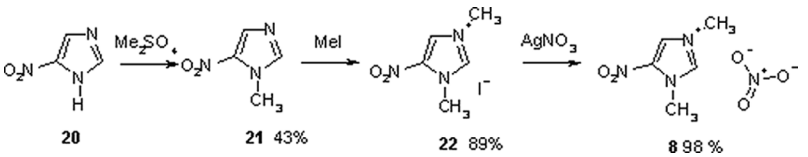
19 7

Scheme 1. Synthesis of PETN **7**.

a 1:1 (w/w) ratio (Scheme 1). Note that the reaction is sensitive to concentration of nitronium ion; if 86% H_2SO_4 is used instead of 96%, a mixture of the trinitrate and tetranitrate will be obtained. Scale-up of the procedure to provide 50–100 g is facile; Camp et al. [30] have previously described kilogram-scale synthesis.

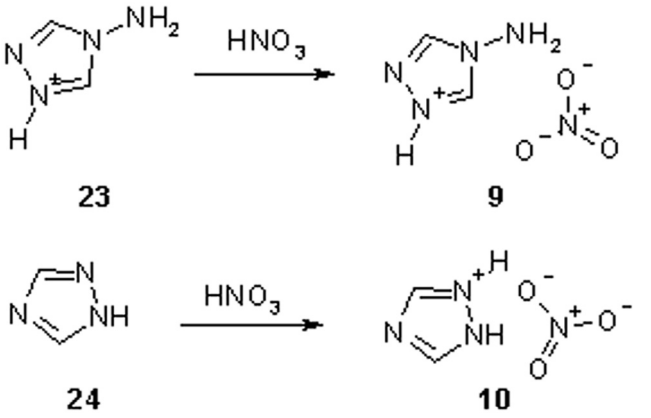
Preparation of heterocyclic nitrate salts **8**–**10** Imidazolium nitrate salt **8** was prepared in 37% overall yield by the alkylation reaction of 5-nitroimidazole **20** with dimethyl sulfate, followed by quarternization of the obtained intermediate **21** with methyl iodide and further treatment of the corresponding salt **22** with silver nitrate (Scheme 2) The initial methylation step gave only a moderate yield (43%). The addition of a second methyl group proceeded more smoothly providing **22** in 89% yield. Reaction of **22** with silver nitrate gave **8** in near quantitative yield (98%).

Two triazolium nitrate salts **9** and **10** were obtained in high yields, 89 and 93% respectively, by the treating the corresponding heterocycles with concentrated nitric acid in dry methanol under nitrogen flow at room temperature for 1 h (Scheme 3).



20 21 43% 22 89% 8 98 %

Scheme 2. 1,3-Dimethyl-4-nitroimidazolium nitrate salt **8**.



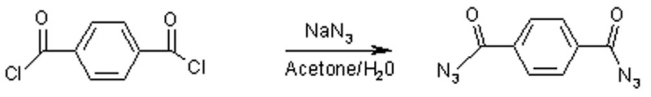
23 **9**

24 **10**

Scheme 3. Triazolium nitrate salts **9** and **10**.

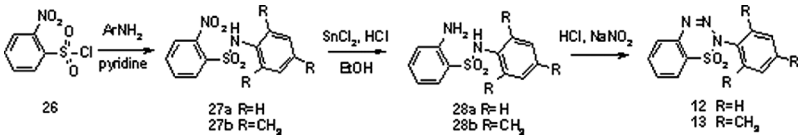
Synthesis of terephthaloyl azide **11** The reported synthesis of terephthaloyl azide (**11**) from the acyl hydrazine (prepared from the corresponding methyl ester) with dinitrogen tetroxide [39] is limited by the cost and hazards of dinitrogen tetroxide. We found an efficient alternative synthesis in the simple nucleophilic displacement of chloride from **25** by sodium azide providing terephthaloyl azide (**11**) in 81% yield (Scheme 4).

Preparation of 2-substituted benzo[1,2,3,4]thiatriazine-1,1-dioxides **12**–**13** Following a modification of Ullmann's method [22], we prepared 2-phenylbenzo[1,2,3,4]thiatriazine-1,1-dioxide (**12**) from 2-nitrosulfonyl chloride (**26**) (Scheme 5): a condensation of the sulfonyl chloride with aniline first gave sulfonamide **27a** in 82% yield. Baeyer reduction of the nitro



25 **11**

Scheme 4. Synthesis of terephthaloyl azide **11**.



Scheme 5. Synthesis of 2-aryl[1,2,3,4]thiatriazine-1,1-dioxides (**12** and **13**).

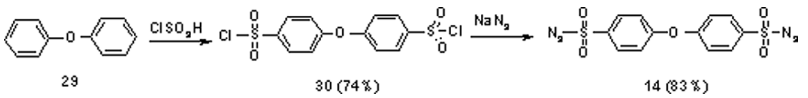
group provided 2-amino-*N*-phenylbenzenesulfonamide (**28a**) in 92% yield, which was subjected to HONO-mediated ring-closure to provide **12** in 75% yield.

Similarly, **13** was prepared in 74% yield from **28b**, which was obtained in 82% yield from **27b**. Sulfonamide **27b** was prepared in 70% yield from 2-nitrosulfonyl chloride (**26**) (Scheme 5).

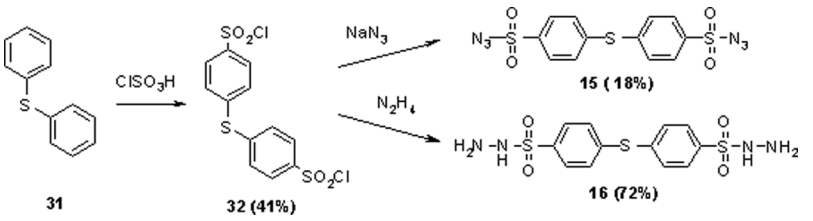
Blowing agents **14**–**16** *derived from disulfonyl dichlorides* Both disulfonyl azides **14** [24] and **15** and disulfonylhydrazine **16** [25] were prepared by the cited literature methods, from the respective disulfonyl dichlorides **30** and **32**, which are accessible from diphenyl ether (**29**) and diphenyl sulfide (**31**) (Schemes 6 and 7).

Starting from diphenyl ether (**29**), disulfonyl dichloride **30** was prepared in 74% yield (Scheme 6). Reaction of **30** with sodium azide provided disulfonyl azide **14** in 83% yield.

Disulfonyl azide **15** was obtained in 18% yield (Scheme 7) from the disulfonyl dichloride **32**, prepared from diphenyl sulfide (**31**) in 41% yield. Disulfonylhydrazide **16** was obtained in 72% yield from reaction of disulfonyl dichloride **32** with hydrazine.



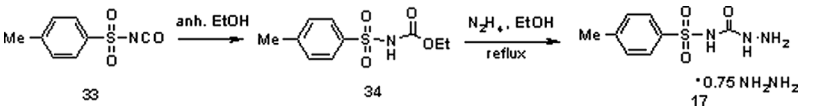
Scheme 6. Bis[4-(azidosulfonyl)phenyl] ether **14**.



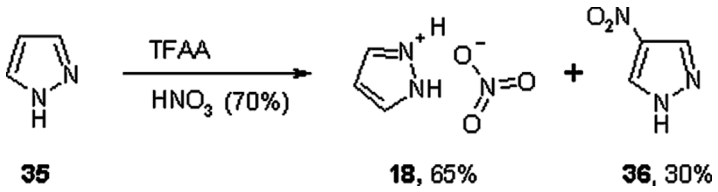
Scheme 7. 4,4′-Thiobis-benzenesulfonyl azide (**15**) and 4,4′-thiobis(benzenesulfonyl hydrazide) **16**.

Synthesis of N-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt **(17)** A facile route to *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt (**17**) proceeds via the intermediate, *N*-ethoxycarbonyl-(4-methylphenyl)sulfonamide (**34**), prepared from *p*-tolylsulfonyl isocyanate (**33**) (Scheme 8). Intermediate **34** was prepared in 92% yield by the reaction of absolute ethyl alcohol with *p*-tolylsulfonyl isocyanate (**33**) at −20°C. Conversion of the carbamate **34** to semicarbazide hydrazine salt **17** (82% yield) occurred by reaction with 2 molar equivalents of hydrazine monohydrate in refluxing ethanol.

Preparation of pyrazolium nitrate **18** Surprisingly few azole energetic salts are reported in the literature; most reported examples are limited to imidazolium, triazolium, or tetrazolium derivatives [19,20,40]. Treatment of pyrazole **35** with excess trifluoroacetic anhydride and 70% nitric acid provided pyrazolium nitrate (**18**) in 65% yield (Scheme 9) along with 4-nitropyrazolium nitrate (30%). The last readily decomposes to 4-nitropyrazole (**36**) on silica gel. Increasing the concentration of nitric acid to 90% gives in a 61% yield of



Scheme 8. Synthesis of *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide (0.75 N_2H_4) **17**.



Scheme 9. Preparation of pyrazolium nitrate **18**.

4-nitropyrazole (**36**). Pyrazolium nitrate (**18**) is, of course, easily prepared simply from nitric acid and pyrazole.

Pyrazolium nitrate crystallizes from ethyl acetate as thin needles in the monoclinic space group $P2_1/c$. Figure 3 (top) shows the contents of the asymmetric unit, along with bond lengths and angles. The pyrazolium cation and nitrate anion are almost coplanar (angle between meanplanes = 16.8(2)°). Also shown in Fig. 3 is the way the salt assembles about a crystallographic center of inversion with two nitrates bridging two pyrazolium cations by means of a network of hydrogen bonds. These coplanar dimeric units stack through π–π interactions along the short *a* axis and are further interconnected by weaker C−H···O contacts. Crystalline pyrazolium nitrate (**18**) has a density of 1.595 g·cm^{-3}.

Synthesis of cyclic tertiary amines **38**, **42** Previously reported compounds of type **38** were made by cyclization reaction of the corresponding diamines with formaldehyde [34,35]. An efficient access to *N*,*N*-unsymmetrically substituted **38** was developed in our group using the cyclocondensation property of benzotriazole to conduct the hexahydropyrimidine [41] or imidazolidine [42] ring system and its good leaving group ability in nucleophilic substitutions [43] to perform *N*-functionalization. Surprisingly, only one literature example was published for the synthesis of five-, six-membered tertiary 1,3-diamine by the reduction of the corresponding cyclic ureas with LAH in ether at room temperature for 1 h in 50–58% yields [44], which was not reproducible in our hands. Tertiary cyclic amines based on the stable pyrrolidine ring can be obtained by the *N*-alkylation

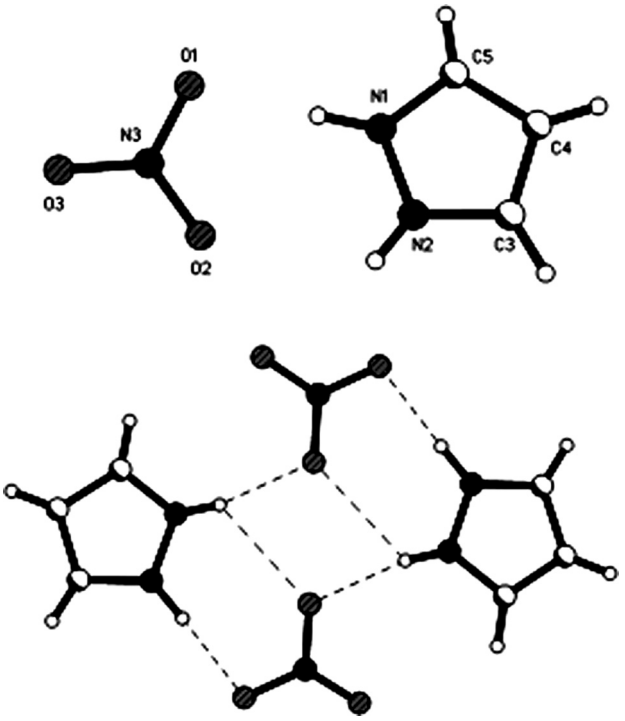
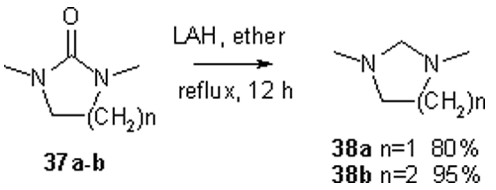


Figure 3. X-Ray crystal structure of (**18**); top: contents of the asymmetric unit, bottom: the dimeric assembly of two asymmetric units, controlled by multiple hydrogen bonding interactions. Bond lengths (Å) and angles (°): N1−C5 1.342(3), N1−N2 1.345(3), N2−C3 1.339(3), C3−C4 1.380(3), C4−C5 1.389(3), N3−O3 1.247(2), N3−O1 1.265(2), N3−O2 1.275(2), C5−N1−N2 108.4(2), C3−N2−N1 109.2(2), N2−C3−C4 108.2(2), C3−C4−C5 105.9(2), N1−C5−C4 108.2(2), O3−N3−O1 121.3(2), O3−N3−O2 120.7(2), O1−N3−O2 118.0(2).

reaction of pyrrolidine in 33% yield [45] or by the reduction reaction of the respective pyrrolidones with $BH_3 \bullet THF$ [46] or 9-borabicyclo[3.3.1]nonane [47]. Each of the available methods suffers some disadvantages: low yield, complicated isolation conditions due to high solubility in water, low boiling point and



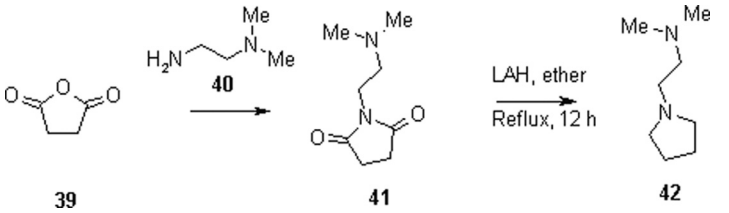
Scheme 10. Preparation of 1,3-dimethyl-imidazoline **38a** and -hexahydropyrimidine **38b**.

stability of products, and cost and availability of starting materials. These problems prompted a new search for general, milder, more convenient reaction conditions for preparation of cyclic tertiary amines. We now employ a reduction reaction involving cyclic carbonyl compounds **37**, **41** to access the imidazolidine, hexahydropyrimidine, and pyrrolidine derivatives **38**, **42**.

1,3-Dimethylimidazoline **38a** and 1,3-dimethylhexahydropyrimidine **38b** were synthesized by the reduction of the corresponding cyclic ureas **37a-b** with 1.15 molar equivalents of LAH in ether under reflux for 12 h in 80–95% yield (Scheme 10).

N,N-Dimethyl-2-(1-pyrrolidinyl)-1-ethanamine **42** was obtained in 87% yield by the reaction of 2.3 molar equivalents of LAH and 1-[2-(dimethylamino)ethyl]dihydro-1*H*-pyrrole-2, 5-dione **41** in ether under reflux for 12 h. Intermediate **41** was prepared by treatment of succinic anhydride **39** with dimethylaminoethylamine **40** in a microwave synthesizer at 100 watts and 130°C for 5 min followed by distillation to give succinimide **41** in 59% yield. This method provides the use of cheap starting materials, good to excellent yields (80–95%), and better conditions for isolation of the desired products **38**, **42** by evaporating ether under reduced pressure (Scheme 11).

Ignition Delay of Cyclic Tertiary Amines **38**, **42** Ignition delay is a main criterion in the selection of hypergolic bipropellants and its long value is attributed to ''hard start'' in thrust engines that may cause rapid dismemberment of engine hardware. Consequently, a study of ignition delays by a



Scheme 11. Synthesis of *N*,*N*-dimethyl-2-(1-pyrrolidinyl)-1-ethanamine **42**.

modern screening technique [29] allows a better understanding about the mechanism of hypergolic ignition. Our choice to synthesize cyclic tertiary amines **38a**,**b** and **42** is based on their following properties, which are considered as important factors influencing ignition delays [48]: high basicity, high weight percent of nitrogen (19.69–27.97%), connection of two nitrogen atoms to each other by short aliphatic linkages, and low steric hindrance of substituent at N atoms. Although compounds **38a**,**b** and **42** exhibit relatively long ignition delays (45–76 μs) in comparison with its value for monomethylhydrazine (10.6 μs), they are promising components of blended hypergolic fuels.

Thermogravimetric Analyses and Differential Scanning Calorimetry

DSC-TG analysis of pentaerythritol tetranitrate, **7** DSC analysis performed on 2.9925 mg of PETN (**7**) showed a sharp loss in mass (52%) at 175°C and also indicated a large exothermic peak (+32 mW) at ∼180°C (Fig. 4). Calculation of the generated heat flow per mmol is determined to be +3.38 W/mmol. PETN (**7**) is an excellent blowing agent candidate.

DSC-TG Analyses of Heterocyclic Nitrate Salts **8**–**10**

Thermogravimetric analysis of 1,3-dimethyl-4-nitroimidazolium nitrate salt, **8** TG analysis (obtained with 0.248 mg of **8** heating from 50 to 1100°C with rate of 10°C/min.) showed a sharp and

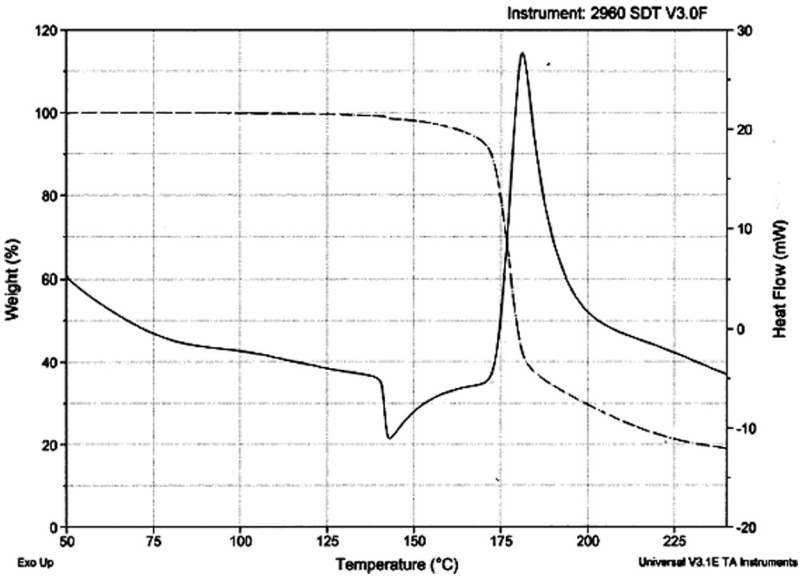


Figure 4. DSC-TGA of blowing agent **7**.

drastic decrease (60%) in mass at 180°C (Fig. 5). Since off-gassing is rapid and falls near 180°C, 1,3-dimethyl-4-nitroimidazolium nitrate salt **8** is also a good blowing candidate.

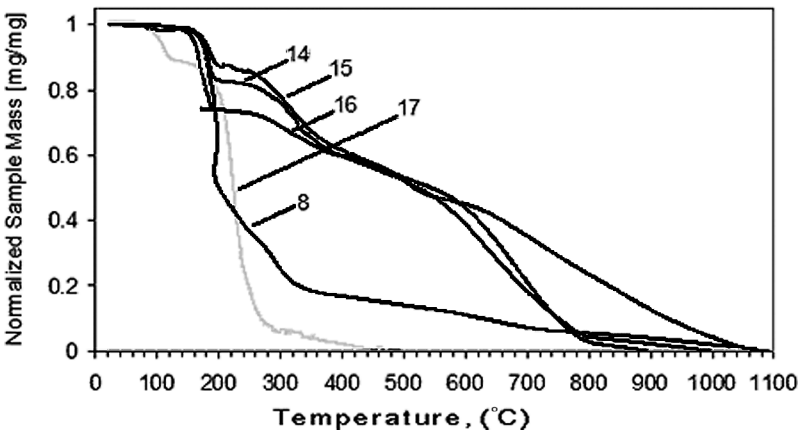


Figure 5. TGA of blowing agents **8**, **14**–**17**.

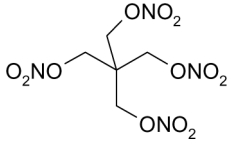
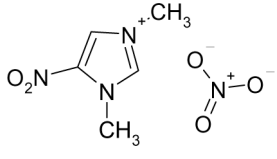
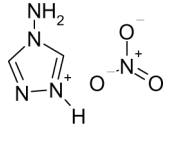
DSC-TG analyses of heterocyclic nitrate salts, **9–10** DSC-TG analyses performed on 3.1346 mg of (**9**) and 2.5601 mg of (**10**) eachshowed a decline in mass at ∼175°C, indicated by a broad exothermic peak (+6 mW) at 80°C and (+ 5 mW) at 160°C, respectively. However, because nitrate salts **10** showed a DSC gas evolution ∼180°C but did not rapidly generate gas, 1,2,4-triazolium nitrate **10** is not a good candidate for blowing agents but may be considered for other energetic formulations. 4-Amino-1,2,4-triazolium nitrate **9** is considered a poor blowing agent candidate due to its melting point of 67–68°C.

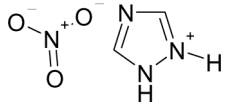
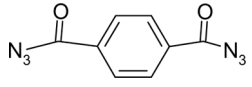
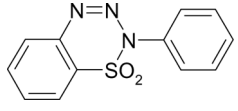
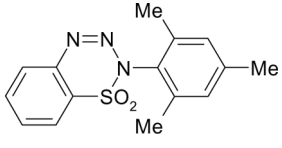
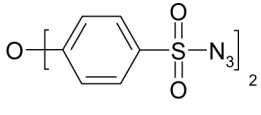
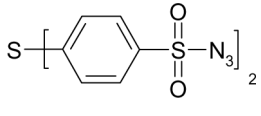
Thermogravimetric analysis of terephthaloyl azide, **11** Thermogravimetric analysis (TGA) (50 to 200°C, rate: 10°C/min) performed on a 0.817-mg sample of **11** showed a sharp and drastic decrease (98% loss) in mass starting at 105°C and ending at 117°C (Table 1). These TDA data do not fit our requirement gas evolution ∼180°C; however, since **11** generates gas quickly, is shock stable, and has a high melting point of 105–106°C, terephthaloyl azide (**11**) is a good candidate for other energetic formulations.

Thermogravimetric analyses of 2-substituted benzo [1,2,3,4]thiatriazine-1,1-dioxides, **12** *and* **13** TG analysis (50 to 300°C, rate: 20°C/min) of benzo[1,2,3,4]thiatriazine-1,1-dioxides (**12**, 1.545 mg; **13**, 0.783 mg) showed a trend of gradual decomposition. 2-Phenylbenzo[1,2,3,4]thiatriazine-1,1-dioxide **12** showed the sharpest loss in mass, losing 30% of its mass from 210 to 265°C. Thiatriazine **13** decomposed in stages starting from 100°C with plateaux from 110–130°C and 140–190°C. Overall, compounds **12–13** are poor blowing agent candidates, since samples required heating to 260°C before 30% mass loss was achieved.

Thermogravimetric analyses of disulfonyl azides **14** *and* **15** *and disulfonylhydrazine,* **16** TGA data (obtained with 1.755 mg of **14** heating from 50 to 1100°C with a rate of 10°C/min) show that as temperature increases, a gradual decline in mass begins from ∼150°C and ends at ∼185°C with a total loss in mass of 17%

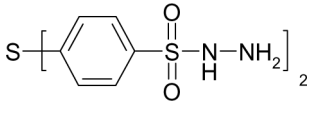
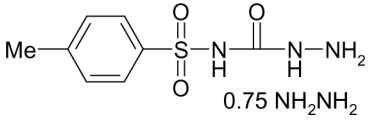
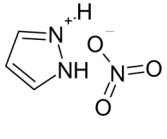
Table 1
Melting point and thermogravimetric data for compounds **7**–**18**

	Structure	Mp (°C)	Decomposition onset (°C)	% Mass loss at 180°C (%)	Impact sensitivity[a]
7		140	175	60	Explosive
8		162–163	175	65	—
9		67–68	165	7.5	—

10		137–138	160	25	—
11		105–106	105	98	Explosive
12		110–111	100	3	—
13		163–165	120	6	—
14		84–86	140	14	—
15		75–77	140	12	—

(*Continued*)

Table 1
Continued

	Structure	Mp (°C)	Decomposition onset (°C)	% Mass loss at 180°C (%)	Impact sensitivity[a]
16		162	140	22	—
17		136–139	190	25	—
18		147–148	120	95	—

[a]Impact sensitivity measurements were carried out by hitting with hammer (weight 750 g) from 100 cm for sample (5–10 mg). Five impact trials were conducted for each compound (**7**–**18**) and any one or more explosive events were considered as "explosive."

corresponding to the expected loss of two molecules of N_2 per molecule of blowing agent **14** (Table 1, Fig. 5). Since off-gassing is rapid and falls near 180°C, **14** is a good blowing agent candidate.

The TGA run conducted with 4.356 mg of disulfonyl azide **15** closely resembles that of **14** (Table 1). The loss of mass (15%, roughly 2 molecules N_2 per molecule **15**) was gradual, starting around 155°C and ending at ~195°C. Behaving similarly to **14**, disulfonyl azide **15** is also a promising blowing agent candidate (Fig. 5).

It was observed that 4,4′-thiobis(benzenesulfonyl hydrazide) (**16**) simultaneously melts and off-gasses at 162°C. This rapid off-gassing, however, was not as strongly evident in the TGA, which displays only a slightly more rapid decrease in mass with heating (a 25% loss over a range of 130–185°C) as compared to **14** and **15** (Fig. 5). Moreover, the decomposition occurs at a lower temperature than expected.

Thermogravimetric analysis of N-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt, **17** TGA performed on *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt (**17**) showed two distinctive regions, an area starting around 100°C, indicating loss of hydrazine, and a second area showing a decline in mass at ~190° C due to decomposition (Fig. 5). DSC analysis (50 to 300°C, rate: 10°C/min) performed on *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt **7** showed a large endothermic peak between 120 and 145°C, which represents a melting. A number of reactions occurred above 150°C that appeared as two DSC peaks maximum at 155 and 175°C and one DSC peak minimum at 165°C and led to gas evolution indicated by a large exothermic peak starting at ~190°C and ending at ~220°C. Since decomposition of this material is sharp, occurs near 180°C, and nearly 90% of the mass is lost during the decomposition, **17** is an excellent blowing agent candidate.

DSC-TGA of pyrazolium nitrate, **18** DSC analysis of 0.3725 mg of the nitrate salt **18** shows a decline in mass at 120°C;

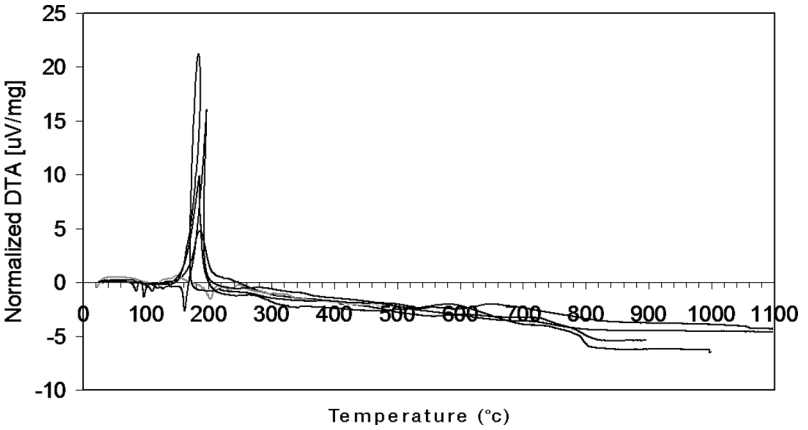


Figure 6. DTA of blowing agents **8**, **14**–**17**.

however, a DSC peak maximum does not occur until 168°C and indicates a broad exothermic peak (+ 5 mW) starting at 152°C and ending at 210°C. The calculated heat flow for the nitrate salt is +0.35 W/mmol. A larger sample (1.45 mg), which was taken for retesting, shows the same value of temperature for the decline in mass and the DSC peak maximum.

Differential thermal analysis (DTA) of materials **8**, **14**–**17** DTA analysis performed on compounds **8**, **14**–**17** showed that all these materials begin decomposing at 180°C and underwent largely exothermic reactions around 180°C. Because gas evolution is rapid and occurs near 180°C, 1,3-dimethyl-5-nitroimidazolium nitrate salt (**8**), disulfonyl azides (**14**,**15**), disulfonylhydrazine (**16**), and *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt (**17**) are promising blowing candidates (Fig. 6).

Conclusions

Twelve energetic additives **7**–**18** were evaluated for use as blowing agents. TGA/DTA/DSC testing of materials **7**–**18** showed that among leading candidates **7**, **8**, **14**–**17**, pentaerythritol tetranitrate **7**, and *N*-(hydrazinocarbonyl)-4-methylbenzenesulfonamide hydrazine salt **17** are the most promising. Compounds **10**–**11** are

good materials for other energetic formulations. The rest of the materials **9**, **12**, **13**, and **18** are poor blowing agent candidates. As for the development of new methodologies for hypergolic compounds, an improved and efficient method has been developed for preparation of cyclic tertiary amines **38**, **42** that provides an easy access to the discovery of new hypergolic compounds.

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