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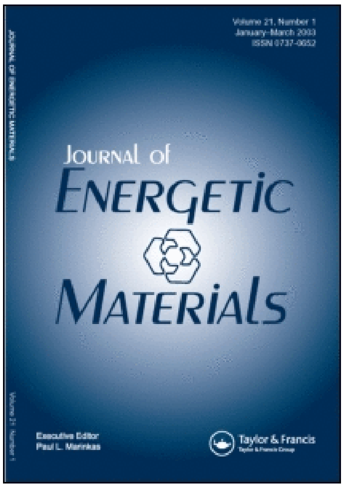

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Decomposition of Azo- and Hydrazo-Linked Bis Triazines

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Decomposition of Azo- and Hydrazo-Linked Bis Triazines

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In a search for novel energetic materials, azo-linked bis triazines were pursued. Herein the thermal decomposition of 14 simple triazines and 16 hydrazo- or azo-linked bis triazines were studied using mass spectrometry, permanent gas evolution, and differential scanning calorimetry. At temperatures far above the melting/decomposition point, decomposition was complete. Lower temperatures provided insight into the stability of the functional groups pendant to the triazine rings. Decomposition gases were identified by chromatography; they indicated little degradation of the triazine rings. The s-triazine ring system appears very stable, resisting decomposition up to 550°C while its substituents undergo relatively isolated chemistry.

Keywords: azo bis triazines, hydrazo bis triazines, thermal decomposition

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Introduction

Since the discovery of 2,4,6-trinitrotoluene over a century ago, nitration of aromatic carbon ring systems has been thoroughly exploited. In an effort to construct more energetic yet stable

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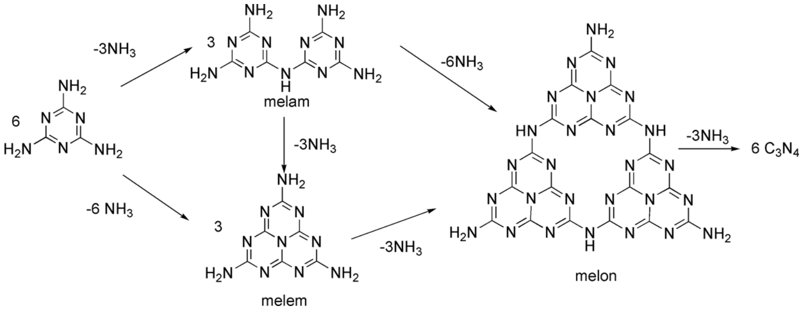
species, carbon backbones [1,2] have been abandoned in favor of high-nitrogen, heterocyclic rings [3–6]. These compounds derive their energy from large positive heats of formation and large amounts of gas released rather than the oxidation of a carbon backbone. Unfortunately, nitration of high-nitrogen heterocycles is difficult to effect and has not resulted in stable compounds [7]. Unlike other heterocyclic rings—e.g., tetrazines and tetrazoles [8,9]—*s*-triazine is quite stable; it tends to undergo depolymerization before catastrophic decomposition [10].

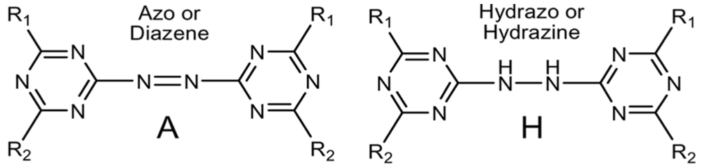
s -Triazine, containing over 50% nitrogen, is an intriguing heterocyclic for energetic materials. Triazine rings have been studied for use in a number of applications—herbicides, pool chemicals, synthesis, and polymers. Melamine, 2,4,6-triaminotriazine, one of the most ubiquitous triazines is prepared by the thermolysis of cyanamide or ammonium dicyanamide [11]. Differential scanning calorimetric (DSC) analysis of melamine shows two endothermic regions: one at melting point 350–400°C and the other at 450–500°C. Heating above its melting point resulted in thermal condensation, losing ammonia to form melam and melem. The formation of melam requires only elimination of some substituents, whereas a more condensed form, melem, requires breaking the aromatic system (Scheme 1) [12]. The strong participation of the nitrogen lone pairs in the pi-system renders both essentially non-basic [13].



Scheme 1. Thermal aminolysis of melamine to form condensed structures.

Energetic triazines are not new. Triazido triazine, easily synthesized from sodium azide and cyanuric chloride, was reported as early as 1921. Although it is too sensitive for use in a commercial energetic application, small quantities have been employed to produce carbon or carbon nitride nanomaterials [14,15]. Its decomposition is known to produce nitrogen gas and, depending on the conditions, cyanogens $(CN)_2$ and C_3N_4 powders [16].

In general, the higher the molecular weight, the more thermally stable the compound. Therefore, we have been interested in the possibility of using linked triazines in energetic



ID	Linkage	R_1	R_2	MW	% Nitrogen
H-1	-NH-NH-	-OMe	-OMe	310.3	36.1
A-1	-N=N-			308.3	36.4
H-2	-NH-NH-	-Cl	-Cl	327.9	34.2
A-2	-N=N-			325.9	34.4
H-3	-NH-NH-	$-NH_2$	-Cl	289.1	48.5
A-3	-N=N-			287.1	48.8
H-4	-NH-NH-	$-NH_2$	-OMe	280.3	50.0
A-4	-N=N-			278.2	50.3
H-5	-NH-NH-	$-NH_2$	$-NH_2$	250.2	67.2
A-5	-N=N-			248.2	67.7
H-6	-NH-NH-	$-NH_2$	$-NHNH_2$	280.3	70.0
H-7	-NH-NH-	$-NHNH_2$	$-NHNH_2$	310.3	72.2
H-8	-NH-NH-	$-NH_2$	$-N_3$	302.2	74.2
A-8	-N=N-			300.2	74.7
H-9	-NH-NH-	$-N_3$	$-N_3$	354.2	79.1
A-9	-N=N-			352.2	79.5
Hydrazobenzene	-NH-NH-	-Ph	-Ph		
AzoBenzene	-N=N-				

Figure 1. Azo- and hydrazo-linked bis triazines used in this study.

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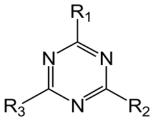

Name	R$_1$	R$_2$	R$_3$	MW	% Nitrogen
Triazine	-H	-H	-H	81.1	51.8
Cyanuric Acid	-OH	-OH	-OH	129.1	32.6
Cyanuric Chloride	-Cl	-Cl	-Cl	184.4	22.8
Chloro diamino triazine	-Cl	-NH$_2$	-NH$_2$	145.6	48.1
Chloro dimethoxy triazine	-Cl	-OMe	-OMe	175.6	23.9
Amino dimethoxy triazine	-NH$_2$	-OMe	-OMe	156.1	35.9
Trimethoxy triazine	-OMe	-OMe	-OMe	171.2	24.6
Hydrazino dimethoxy triazine	-NHNH$_2$	-OMe	-OMe	171.2	40.9
Dihydrazino methoxy triazine	-NHNH$_2$	-NHNH$_2$	-OMe	171.2	57.3
Melamine	-NH$_2$	-NH$_2$	-NH$_2$	126.1	66.6
Hydrazino diamino triazine	-NHNH$_2$	-NH$_2$	-NH$_2$	141.1	69.5
Dihydrazino amino triazine	-NHNH$_2$	-NHNH$_2$	-NH$_2$	156.2	71.8
Trihydrazino triazine	-NHNH$_2$	-NHNH$_2$	-NHNH$_2$	171.2	73.7
Triazido triazine	-N$_3$	-N$_3$	-N$_3$	204.1	82.4
Phenylhydrazine	-NHNH$_2$	--	--	108.1	25.9

Figure 2. *s*-triazines used in this study.

formulations. Incorporation of a nitrogen linkage was postulated to decrease sensitivity and increase energy [3,17]. Herein we examined the relative stabilities of triazinyl hydrazines and diazenes (hydrazo and azo-linked bis-triazines) with various substituents (Fig. 1). For comparison azobenzene and hydroazobenzene and single trisubstituted triazine rings were examined in an analogous fashion (Fig. 2).

Experimental Section

Samples to be thermolyzed (0.1 to 3 mg) were placed in glass capillary melting-point tubes (Kimax 1.5–1.8 × 45 mm) that had been presealed at one end. The capillaries were sealed under vacuum (~5 mm Hg) to produce a vessel about 40 µL in volume and 35 mm in length. Depending on the temperature desired and time needed, the capillary tubes were heated in a Mel-Temp^{TM} (Barnstead/Thermolyne, Dubuque, IA) melting point device, an oven, or a tube furnace. The oven and tube furnace were brought to the desired temperature before the sample was introduced. Because the azido compounds would explode if instantly heated to their decomposition temperature, the capillaries containing the azido compounds were slowly heated in the melting point device to visualize the decomposition and then placed in the muffle furnace when the bubbling had subsided.

Triazines heated in the presence of solvents were prepared in a fashion similar to those thermolyzed neat. Samples (5 to 10 mg) and solvent (~25 µL) were added directly into glass capillary tubes via syringe. Samples ranged from slurries to homogenous solutions. Sealing of the tubes was performed at ambient pressure, and the tubes usually contained some headspace. All heating was performed in an oven, and samples were heated for 1 h at 300°C. After heating, the capillaries were frozen in liquid nitrogen and, when broken, quickly inserted into a GC vial (due to gases produced, much of the sample was expelled from the capillary during warming). The vial was filled with HPLC-grade chloroform, shaken, and sonicated for 10 min before analysis. Samples ranged from homogenous solutions to cloudy suspensions.

Triazine decomposition gases were identified using a 5890 series II gas chromatograph with a thermal conductivity detector (GC/TCD) fitted with an Alltech Hayesep DB 100/120 column ($30' \times 1/8'' \times 0.085''$ stainless steel). Helium was used as the carrier gas. The column head pressure was kept at 40 psi, the column flow was 20 mL/min, and the reference flow was 50 mL/min. The inlet temperature was not regulated. The oven program was as follows: 30°C isothermal for 10 min, ramp 20°C/min to 180°C and hold for 17.5 min, to give a total run time of 35 min. The detector was maintained at 200°C in positive polarity. The GC system utilized two six-port valves and three compressed gas tanks. Valve 1 alternatively flowed the carrier gas or helium purge through a section of Tygon tubing ($\sim 12'' \times 3/8''$) that could be opened to insert capillaries (which were then broken individually during GC runs). The carrier gas then passed to valve 2, which was fitted with standard size gas loops (25, 50, 100, 250, 500, and 1000 µL) through which a standard gas mixture could be flowed. Valve 1 was internal and

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pneumatically operated by compressed air and actuated by the HP Chemstation software, and valve 2 was manually operated by the researcher. Calibration curves were constructed from a standardized mixture (Scott Specialty Gases, Plumstead, PA) of N_2 (40.01%), CO (5.01%), CO_2 (29.99%), and N_2O (24.99%) in addition to pure methane and difluoroethane.

Condensed-phase products were identified using a 5890 series II gas chromatograph with a mass selective detector (GC/MS) (Hewlett Packard, Palo Alto, CA) fitted with an Agilent Technologies HP-5MS column ($30\,m \times 0.25\,mm \times 0.25\,\mu m$ film) (Agilent Technologies, Santa Clara, CA). Helium was used as the carrier gas and held at a constant flow of 10 mL/min. The inlet was split with a 2 mL/min flow, and the temperature was kept at 250°C. The oven program was as follows: 70°C isothermal for 2 min, ramp 10°C/min to 150°C, then 20°C/min to 280°C, and hold for 3.50 min to give a total run time of 20 min. A solvent delay of 5 min was required for cyclohexanol samples and 6 min for benzonitrile. The detector was maintained at 300°C and measured m/z 10–400.

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The synthesis of *s*-triazines derivatives has been exploited for over 50 years and many are available commercially. Trivial syntheses are readily available in the literature [18–28]. Dihydrazino methoxy triazine, hydrazino dimethoxy triazine, amino dihydrazino triazine, diamino hydrazino triazine, and trimethoxy triazine were synthesized by the Naval Surface Warfare Center, Indian Head Division, Indian Head, Maryland. These compounds were provided to the University of Rhode Island and were used without purification. The preparation of the bis-triazinyl hydrazines and diazenes used in this research is described below.

Preparation of N,N′-Bis-(4,6-Dimethoxy-[1,3,5]Triazin-2-yl)-Hydrazine (H-1)

Hydrazine monohydrate (1.725 g, 34.45 mmol) was added slowly to a solution of chlorodimethoxytriazine (12.1 g, 68.9 mmol), potassium carbonate (9.525 g, 68.9 mmol), and isopropanol (100 mL) with stirring at 50°C. The reaction was fitted with a condenser and kept at 50°C overnight in an oil bath. The initially white opaque solution was given a slight pink tint several hours into the reaction. The reaction was then filtered and washed with water to give a pink tinted solid which became a white powder, **H-1** (yield 10.64 g, 99%), after oven drying. Recrystallized from acetonitrile (5 g/400 mL, 88% recovery). mp: 222–224°C. ^{1}H NMR (200 MHz, DMSO-D$_6$) δ 9.75 (b, 2H, NH-NH), 3.86 & 3.76 (d, 12H, O-CH$_3$); (400 MHz, CDCl$_3$) δ 7.46 (s, 2H, NH-NH) δ 3.97 & 3.92 (d, 12H, O-CH$_3$) ppm. ^{13}C NMR (50 MHz, DMSO-D$_6$) δ 172.2, 171.7, 169.5, 54.376, 54.4, 54.2; (100 MHz CDCl$_3$) δ 173.1 & 172.6, 170.0, 55.2 ppm. IR (ATR) 3250 (s), 2957 (s), 1587 (vs), 1366 (vs), 816 (s) cm^{-1}.

Preparation of Bis-(4,6-Dimethoxy-[1,3,5]Triazin-2-yl)-Diazene (A-1)

To a stirring solution of N-bromosuccinimide (20.4 g, 115 mmol) in acetonitrile (80 mL) was slowly added **H-1** (7.4 g. 23.8 mmol). The white suspension was allowed to stir at room temperature for 2 h as it became a dark orange saturated solution. The reaction was filtered, washed with acetonitrile (2 × 20 mL) and cold water (2 × 20 mL), and dried to give a brown/orange powder **A-1**. Recrystallization from boiling acetonitrile yields large orange needles (overall yield 5.7 g, 77%). mp: 228–232°C dec. ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.15 (s, O-CH$_3$) ppm; (200 MHz, DMSO-D$_6$) 4.06 (s, O-CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ 176.7, 174.1, 56.4 ppm. IR (KBr): 3025, 2954, 1587, 1512, 1477, 1370, 1240, 1108, 1068, 922, 829, 732, 620, 576 cm^{-1}. Anal. Calcd. for $C_{10}H_{12}N_8O_4$: C, 38.96; H, 3.92; N, 36.35. Found: C, 38.78; H, 3.94; N, 36.02.

Preparation of N,N′-Bis-(4,6-Dichloro-[1,3,5]Triazin-2-yl)-Hydrazine (H-2) and Bis-(4,6-Dichloro-[1,3,5]Triazin-2-yl)-Diazene (A-2)

Synthesized similar to the procedure by Loew and Wies [29]. An improved synthesis and purification procedure for **H-2** is now patent pending by the U.S. Navy.

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H-2 ^{1}H NMR (100 MHz, acetone-D$_6$) δ 10.32 (s). ^{13}C NMR (100 MHz, acetone-D$_6$) δ 172.2, 171.3, 168.7. IR (ATR): 3225, 3095, 2960, 1600, 1560, 1530, 1505, 1425, 1385, 1300, 1265, 1245, 1215, 1190, 1005, 860, 800, 750, and 700 cm^{-1}. mp: >250°C.

A-2 ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.8, 174.1; (100 MHz DMSO-D$_6$) 171.0, 170.0, 167.3 (100 MHz, acetone-D$_6$) 171.4, 170.5, 167.9 ppm. mp: 199–203°C.

Preparation of N,N′-Bis-(4-Amino 6-Chloro-[1,3,5]Triazin-2-yl)-Hydrazine (H-3)

A solution of ammonium hydroxide (28 g, 28% solution, 0.23 mol) in water (250 mL) was cooled to 0°C in and ice bath. **H-2** (34 g, 0.10 mol) dissolved in acetone (75 mL) was added dropwise as the temperature increased to 30°C. Following addition, the ice bath was exchanged for a heating mantle and the temperature was brought to 40°C and the reaction allowed to stir for 4 h. The initially bright yellow solution became colorless and then slowly developed a white precipitate during the course of the reaction. The reaction was cooled, filtered, and washed free of salts and starting material with water (3 × 200 mL) and acetone (2 × 100 mL). Keeping the reaction temperature near 40°C and the use of only slightly more than 2 equivalents of ammonia will insure that the tetra amino product is not formed. The white solid is dried under vacuum to give **H-3** (28 g, 82%). mp: >350°C. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 9.60 & 9.52 (asy. d, 2H, NHNH) 7.48 & 7.60 (asy. d, 4H, NH$_2$) ppm. ^{13}C NMR δ (100 MHz, DMSO-D$_6$) δ 170.0, 168.9, 168.0 & 167.8, 167.2 ppm. IR (ATR): 3479, 3310, 3131, 2937, 1516, 1362, 1292, 984, 908, 797 cm^{-1}.

Preparation of Bis-(4-Amino 6-Chloro-[1,3,5]Triazin-2-yl)-Diazene (A-3)

To a stirring suspension of **H-3** (3.06 g, 10.5 mmol) in acetonitrile (40 mL) was added N-bromosuccinimide (7.52 g, 42 mmol) in one portion. The opaque white suspension became light brown over several minutes and was deemed complete by visual

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inspection after all the white starting material had been consumed, usually 3 h. The reaction was allowed to stir an additional hour and was then filtered and washed with acetonitrile (2 × 20 mL) and water (2 × 20 mL) to give **A-3** as a dark tan solid (2.69 g, 88%). Very limited solubility in most organic solvents. mp: >360°C. ^{1}H NMR (400 MHz DMSO-D$_6$) δ 8.68 (s, NH$_2$) ppm. ^{13}C NMR (100 MHz DMSO-D$_6$) δ 173.0, 169.6, 168.4 ppm. IR (ATR): 3432, 3307, 3223, 1627, 1557, 1486, 1349, 1298, 1201, 1037, 927, 815 cm^{-1}. Anal. Calcd. for $C_6H_4Cl_2N_{10}$: C, 25.10; H, 1.40; N, 48.79. Found: C, 25.51; H, 1.73; N, 47.80.

Preparation of N,N′-Bis-(4-Amino 6-Methoxy-[1,3,5]Triazin-2-yl)-Hydrazine (H-4)

To a stirring solution of methanol (200 mL), water (100 mL), and sodium hydrogen carbonate (2.6 g, 31 mmol, 2.25 eq.) was added **H-3** (4.0 g, 13.8 mmol). The initially white opaque suspension was heated to reflux and became clear and yellow over the course of 5 h. The yellow solution was hot filtered through glass and rotovapped to 1/30th the volume. The remaining suspension was cooled in the refrigerator, filtered, and the solid was washed free of salts with water (3 × 10 mL) to yield **H-4** (2.5 g, 65% yield). mp: 280°C dec. ^{1}H NMR (400 MHz DMSO-D$_6$) δ 8.91, 8.85, 8.79 (b-m, 1.8H, NHNH) 6.98 & 6.84 (b-d, 3.8H, NH$_2$) 3.75 & 3.68 (b-d, 6H, CH$_3$) ppm. ^{13}C NMR (100 MHz, DMSO-D$_6$) δ 171.2, 170.6, 169.0–168.5 (m) 167.9, 53.3 ppm. IR (ATR): 3508, 3368, 3208, 2957, 1538, 1456, 1364, 1100, 810 cm^{-1}.

Preparation of Bis-(4-Amino 6-Methoxy-[1,3,5] Triazin-2-yl)-Diazene (A-4)

To a stirring solution of **H-4** (1 g, 3.57 mmol) in acetonitrile (25 mL) was added N-bromosuccinimide (2.54 g, 14.3 mmol). The white suspension slowing resulted in a dark orange opaque suspension deemed complete over 4 h when no white starting material remained. The reaction was filtered and washed with

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acetonitrile (25 mL), water (25 mL), and acetone (25 mL). The product was then air-dried to give **A-4** (yield 0.94 g, 94%). mp: 300°C dec. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 8.06 & 8.03 (d, 4.2H, NH$_2$) 3.93 (s, 6H, CH$_3$) ppm. ^{13}C NMR (100 MHz, DMSO-D$_6$) δ 175.5 (C-N=N), 171.8 (C-OMe), 168.9 (C-NH$_2$), 54.7 (CH$_3$) ppm. IR (ATR): 3445, 3300, 3221, 1515, 1350, 1117, 1047, 820 cm^{-1}.

Preparation of N,N′-Bis-(4,6-Diamino-[1,3,5] Triazin-2-yl)-Hydrazine (H-5)

To a room temperature stirring solution of ammonium hydroxide (35 mL, 31.5 g, 260 mmol) and sodium hydrogen carbonate (11.6 g, 138 mmol) in water (100 mL) was added **H-2** (10.05 g, 30.6 mmol) dissolved in acetone (75 mL). The bright yellow solution became chalky and thick as it was warmed to 65°C. The reaction was allowed to stir overnight at 60–70°C to yield a white suspension. The suspension was filtered and the cake washed free of base and chloride salts with copious amounts of water, washed with acetone, and then dried under vacuum to yield **H-5** (7.2 g, 94%). mp: >360°C. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 8.17 & 8.08 (b asy., 1.7H, NHNH), δ 6.14 & 6.08 (b asy., 8H, NH$_2$). ^{13}C NMR (100 MHz, DMSO-D$_6$) δ 168.5, 167.9 & 167.4 ppm. IR (ATR): 3408, 3277, 3114, 1634, 1524, 1435, 1348, 1019, 805 cm^{-1}.

A preparation of the same product using gaseous ammonia proceeds with similar yield [17].

Preparation of Bis-(4,6-Diamino-[1,3,5] Triazin-2-yl)-Diazene (A-5)

To a stirring solution of NBS (11 g, 64 mmol) in acetonitrile (150 mL) was added **H-5** (4.02 g, 16 mmol) in one portion. The initially white suspension was slowly converted to an orange product with refluxing for 4 h. The reaction removed from heat and the product was allowed to settle. The acetonitrile supernatant decanted and water (500 mL) was added and the suspension was sonicated for 10 min and then allowed

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to settle. Carefully decanting the supernatant reduces filtering time of the very fine particulate, which was oven dried to yield a dark tan solid **A-5** (3.5 g, 88%). mp: >350°C. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 7.18 & 7.11 (b-d, NH$_2$) ppm. ^{13}C NMR (100 MHz, DMSO-D$_6$) δ 175.5, 168.4 ppm. IR (ATR): 3458, 3310, 3120, 1634, 1507, 1347, 1007, 814 cm^{-1}.

Preparation of N,N′-Bis-(4-Amino 6-Hydrazino-[1,3,5]Triazin-2-yl)-Hydrazine (H-6)

To a stirring suspension of **H-3** (10.00 g) in water (250 mL) was added sodium bicarbonate (6.1 g, 2.1 eq.) in one portion. To this white suspension was slowly added hydrazine monohydrate (7 mL, 4 eq.) at room temperature. The reaction was slowly brought to reflux and allowed to stir overnight. The reaction developed a slight yellow/green tone to the clear solution over a white product that was filtered and washed with water (3 × 100) and dried at 50°C to yield **H-6** (9.08 g, 94%). mp: 280°C dec. Direct insertion MS gave a good ion at m/z 280. IR (ATR): 3299, 3137, 2940, 1480, 1344, 1123, 943, 801 cm^{-1}.

Preparation of N,N′-Bis-(4,6-Dihydrazino-[1,3,5]Triazine-2-yl)-Hydrazine (H-7)

To a stirring suspension of **H-1** (5.00 g, 16.1 mmol) in water (250 mL) was added hydrazine monohydrate (25 mL, 515 mmol, 32 eq.). The reaction was heated to reflux and the initially clear suspension of insoluble crystals resulted in a creamy white suspension overnight. The reaction was allowed to cool and was then filtered and washed with water (3 × 100 mL). The white product was then dried at 50°C to give **H-7** (4.75 g, 95%). mp: 290°C. IR (ATR) 3270, 2953, 1516, 1385, 1338, 1070, 937, 801 cm^{-1}. Anal. Calcd. for $C_6H_{14}N_{16}$: C, 23.23; H, 4.55; N, 72.23. Found: C, 23.69; H, 4.93; N, 69.79.

Compound **H-7** has been reported produced directly from **H-2** [30]; however, this procedure is not recommended because the very reactive **H-2** is subject to oligomerization and the addition of the hydrazine yields complex products.

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Preparation of N,N′-Bis-(4-Amino 6-Azido-[1,3,5]Triazin-2-yl)-Hydrazine (H-8)

A 250-mL round-bottom flask was charged with a mixture of acetic acid and water (1:1, v:v, 100 mL) and was cooled to −5°C in a large ice bath. **H-6** (5.0 g, 18 mmol) was slowly added and dissolved to give a clear colorless solution. Sodium nitrite (2.6 g, 2.1 eq.), dissolved in water (10 mL), was added dropwise while keeping the reaction below 0°C. The reaction slowly developed a precipitate over several hours and was allowed to stir with warming to room temperature overnight. The tan suspension was filtered and washed with water (2 × 100 mL) and dried to give **H-8** (4.75 g, 88%). mp: 213°C dec. ^{1}H NMR (400 MHz, DMSO-D_6) δ 7.1 & 7.2 (asy. d, 4H, NH_2) 9.2 ppm (asy. d, 2H, NHNH). ^{13}C NMR (100 MHz, DMSO-D_6): 174.8, 170.3, 168.3. IR: 3445, 3296, 3209, 2183, 2133, 1512, 1375, 1344, 815 cm^{-1}. Anal. Calcd. for $C_6H_4N_{16}$: C, 24.01; H, 1.34; N, 74.65. Found: C, 23.81; H, 1.91; N, 69.49.

Preparation of Bis-(4-Amino 6-Azido-[1,3,5] Triazine-2-yl)-Diazene (A-8)

Compound **H-8** (2.0 g, 6.6 mmol) was added slowly to acetonitrile (50 mL) containing N-bromosuccinimide (2.5 g, 14 mmol). The light tan reaction was allowed to stir overnight to yield a dark orange suspension, which was filtered and washed with acetone (30 mL × 3) to give **A-8** (1.73 g). mp: 220°C dec. ^{1}H NMR (400 MHz, DMSO-D_6) 8.35 & 8.33 ppm (broad d, NH_2). ^{13}C NMR (100 MHz, DMSO-D_6) 174.7, 170.2, 168.3 ppm.

Preparation of N,N′-Bis-(4,6-Diazido-[1,3,5] Triazine-2-yl)-Hydrazine (H-9) and Bis-(4,6-Diazido-[1,3,5]Triazine-2-yl)-Diazene (A-9)

The products were achieved by utilizing the direct displacement of the chlorine substituents of **H-2** with sodium azide and then oxidation with NBS as described by Li et al. [31]. **A-9** was recrystallized in acetone (30 mL/g) to deep orange crystals. The crystals exhibited a melting point at 160°C and decomposed until exploding at about 210°C. ^{13}C NMR (100 MHz, acetone-D_6) 175.7, 172.9 ppm.

Results and Discussion

The importance of the substituents on the triazine ring was evident both from the decomposition products and the relative thermal stabilities of the triazine compounds studied (Tables 1 and 2). Pyrolysis of the selected triazine compounds was conducted neat and in the presence of solvent traps—either cyclohexanol or benzonitrile. Condensed-phase species derived from the triazine ring were difficult to identify. Melamine-like compounds were only occasionally observed by GC/MS. This is not surprising since triazine rings, such as melamine, are known to condense, forming high-molecular-weight chains or lattices, and are extremely insoluble and nonvolatile (Scheme 1).

The decomposition of the triazines was conducted in solvents in an effort to identify intermediate thermolysis products. This technique utilizes the solvent to functionalize decomposition intermediates that would otherwise be unstable or, as is the case with amino triazines, have low solubility and volatility. Benzonitrile and cyclohexanol were chosen for their donating properties and thermal stability at high temperature; heated at 300°C for 24 h they yielded few identifiable products. In most of the thermolyses in cyclohexanol two products exhibiting a maximum m/z fragment of 99 were found. These species were formed in cyclohexanol but not benzonitrile thermolyses, and their formation was independent of the substitution of the triazine rings. One species appears to be a simple oxidation of cyclohexanol ($m/z - 1$ amu) and has a fragmentation pattern similar to cyclohexanol. The second species was observed only in cyclohexanol and only with the triazine compounds containing one or more methoxy substituents. This second species exhibited a base peak of 76, which, to date, has not been identified. Cyclohexyl ether was the primary decomposition product when cyclohexanol was heated to 300°C, thereby introducing a significant amount of water to the decompositions.

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Table 1
Thermal and gas analysis of hydrazo- and azo-linked bis triazines

			DSC results				Permanent gases			
Compound	R_1	R_2	Visible MP	DSC Endo	DSC Exo	Heat J/g	Time/ °C	N_2	CO, CO_2, CH_4, CH_3OH	NH_3^*
A-1	-OMe	-OMe	228–232 dec	245	250	920	5 min + H_2O/ 550	0.77	1.55	–
							1 hr/550	0.77	2.93	–
							5 min/550	0.78	1.15	–
							25 hr/250	0.72	0.35	–
							1 hr/250	0.78	0.16	–
							2 min/MP	0.74	0.20	–
H-1	-OMe	-OMe	222–224 dec	225	230	568	5 min + H_2O/ 550	0.49	1.39	–
							5 min/550	0.44	1.41	–
							25 hr/250	0.05	0.25	–
							1 hr/250	–	0.03	–
							2 min/MP	–	0.00	–
A-2	-Cl	-Cl	199–203	190	none	100	5 min/550	0.49	0.16	trace
H-2	-Cl	-Cl	none	225	none	50	5 min/550	0.25	0.11	trace

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A-3	-NH_2	-Cl	none		280	200	5 min/550	0.71	0.20	trace
H-3	-NH_2	-Cl	none	250	none	100	5 min/550	0.53	0.59	–
A-4	-NH_2	-OMe	char[a]	none	250	643	5 min/550	0.68	0.73	–
							25 hr/300	0.22	0.84	–
H-4	-NH_2	-OMe		none	275	280	5 min/550	0.50	0.79	1.4
							25 hr/300	0.06	0.79	trace
A-5	-NH_2	-NH_2	none	unclear	320	100	5 min/550	0.80	0.16	trace
H-5	-NH_2	-NH_2	none	410	none	100	5 min/550	0.55	0.01	2.4
							1 hr/550	0.59	0.23	2.4
H-6	-NH_2	-$NHNH_2$	280 dec	none	320	170	5 min/550	1.36	0.19	2.9
							1 hr/550	1.32	0.41	4.1
H-7	-$NHNH_2$	-$NHNH_2$	275 dec	none	290	270	5 min/550	2.35	0.35	2.9
							1 hr/550	2.27	0.37	4.2
							25 hr/300	1.07	0.15	trace
A-8	-NH_2	-N_3	char[a]		235	700	5 min/550	3.44	0.02	trace
H-8	-NH_2	-N_3	char[a]		242	900	5 min/550	2.81	0.16	–
							1 hr/550	3.14	0.25	–
A-9	-N_3	-N_3	160[b]	160	222	1300	5 min/550	7.28	0.15	–
							2.5 hr/200	5.97	–	–
H-9	-N_3	-N_3	210 dec	none	222	1200	5 min/550	5.66	0.39	–
							1 hr/550	5.23	0.39	–

(*Continued*)

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Table 1
Continued

			DSC results				Permanent gases			
Compound	R_1	R_2	Visible MP	DSC Endo	DSC Exo	Heat J/g	Time/ °C	N_2	CO, CO_2, CH_4, CH_3OH	NH_3^*
Hydrazo benzene	-Ph	-Ph	125		230	115	5 min/550	0.26	–	trace
Azobenzene	-Ph	-Ph	66–69		450	500	5 min/550	0.47	0.01	–

[a] No visable mp when slowly heated, dropping a tube into the Mel-Temp at or above the DSC exo will yield a visual decomposition.

[b] Boils shortly after melting and continues through the decomposition, rapid heating near causes explosion.

[*] Qualitative quantities only.

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Table 2
Thermal and gas analysis of mono *s*-triazines

				DSC results				Permanent gases			
Compound	R_1	R_2	R_3	Visible MP	DSC Endo	DSC Exo	Heat J/g	Time/ °C	N_2	CO, CO_2, CH_4, CH_3OH	NH_3*
Triazine	-H	-H	-H	71				5 min/550	–	–	–
Cyanuric Acid	-OH	-OH	-OH	none	425 & 450		300	5 min/550		1.06	–
Cyanuric Chloride	-Cl	-Cl	-Cl	146 m 192 dec			50	5 min/550	–	trace	–
Chloro diamino triazine	-Cl	-NH_2	-NH_2	none		260	130	5 min/550	–	trace	–
Chloro dimethoxy triazine	-Cl	-OMe	-OMe	71–74		260	600	5 min/550	–	4.43	–
Amino dimethoxy triazine	-NH_2	-OMe	-OMe	218–221	225	235	300	5 min/550	–	1.29	–
Trimethoxy triazine	-OMe	-OMe	-OMe	135–137		260	300	5 min/550	–	0.45	–

(*Continued*)

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Table 2
Continued

				DSC results				Permanent gases			
Compound	R_1	R_2	R_3	Visible MP	DSC Endo	DSC Exo	Heat J/g	Time/ °C	N_2	CO, CO_2, CH_4, CH_3OH	NH_3*
Hydrazino dimethoxy triazine	-$NHNH_2$	-OMe	-OMe	150 dec	150	225	275	5 min/550	0.31	0.62	trace
Dihydrazino methoxy triazine	-$NHNH_2$	-$NHNH_2$	-OMe	220 dec	220	260	200	5 min/550	0.97	0.19	1.6
Melamine	-NH_2	-NH_2	-NH_2	354	360 & 425		250 & 60	5 min/550	trace	–	0.6
								1 hr/550	trace	–	0.9
Hydrazino diamino triazine	-$NHNH_2$	-NH_2	-NH_2	275 dec	280	300	350	5 min/550	0.50	0.09	1.7
								25 hr/300	0.14	0.00	1.5
								25 hr/250	0.12	0.01	1.3

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Dihydrazino amino triazine	-$NHNH_2$	-$NHNH_2$	-NH_2	290 dec	290	300	170	5 min/550	0.98	0.02	2.1
								25 hr/300	0.43	–	2.3
								25 hr/250	0.25	–	1.7
Trihydrazino triazine	-$NHNH_2$	-$NHNH_2$	-$NHNH_2$	290 dec		300	600	5 min + H_2O/550	1.76	0.03	6.7
								5 min/550	1.32	0.02	4.0
								1 hr/550	1.57	0.03	5.3
								25 hr/250	0.73	0.01	3.9
								1 hr/250	0.52	0.00	0.7
								2 min/MP	0.67	0.01	1.6
Triazido triazine	-N_3	-N_3	-N_3	~90	95	220	1500	5 min/550	4.47	0.07	–
								2.5 hr/200	4.47	–	–
Phenyl-hydrazine	-$NHNH_2$	–	–	–				5 min/550	0.56	–	1.7

*Qualitative quantities only.

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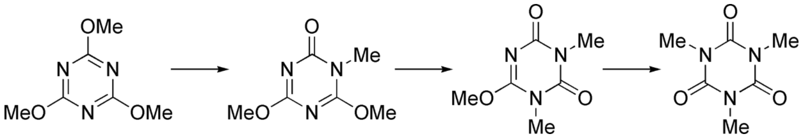
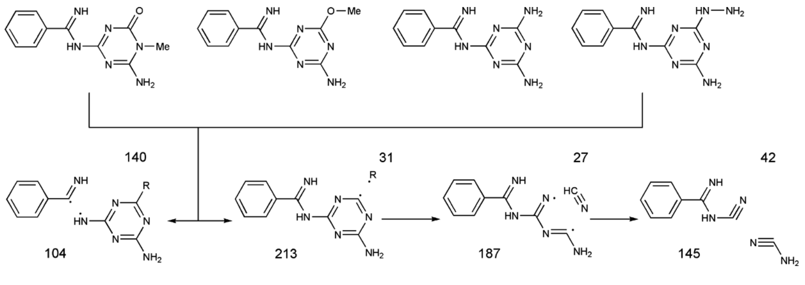


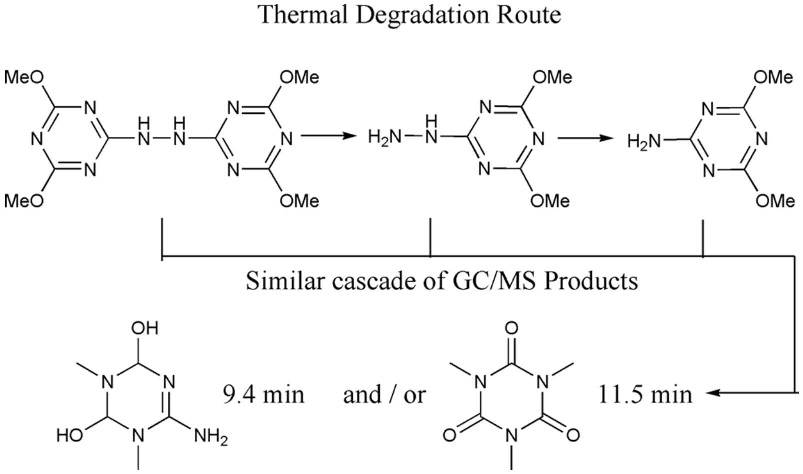
Scheme 2. Rearrangement accompanying methoxy substituents on triazine rings.

Thermolysis of the triazines in benzonitrile formed benzamide and its methylated analogs, N-methyl- and N,N-dimethylbenzamide. These were formed by capturing a methyl during the rearrangement of methoxy substituents. Methoxy triazines are known to undergo rearrangement in the melt or while heated in solvents. The methyl is transferred to a neighboring nitrogen, leaving a ketone functionality behind [32,33]. Thus, trimethoxy triazine formed 1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione as one thermolysis product (Scheme 2). Because this product was also observed with triazines containing only one or two methoxy substituents, some portion of rearrangement is intermolecular.

As discussed below, methoxy and hydrazino substituents are extremely labile. Furthermore, to one amu, they exhibited the same m/z of 31. Therefore, a number of different compounds yielded the same thermolysis products. Naturally, the products detected were only those with sufficient volatility to survive GC/MS analysis. One set of products, at relatively long retention times, were derived from the reaction of benzonitrile with a



Scheme 3. Possible structures and their decomposition via electron impact MS (shown as neutral fragments).



Scheme 4. Thermolysis products including rearrangement (1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione) and decay (6 amino-1,2,3,4-tetrahydro-1,3-dimethyl-1,3,5-triazine-2,4-diol) species.

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triazine species. Scheme 3 suggests a combination of products among various hydrazino compounds followed by fragmentation pathways that result in similar products.

Thermal rearrangement of the methoxy substituents allows for the production of structural isomers. In compounds with more than one methoxy substituent, a number of decomposition products with a similar fragmentation pattern were produced. These similarities are seen in compounds that are proposed to be involved in the decay route (Scheme 4). **H-1** or **A-1** decay to include hydrazino dimethoxy triazine and amino dimethoxy triazine by stepwise degradation, and the decay products from each can be detected in others along the decay route.

Only two triazines were sufficiently stable or sufficiently volatile to be observed by GC/MS at high temperature (550°C)—melamine and cyanuric chloride. In contrast, azido triazines solutions, subjected to moderate temperatures (225°C), yielded no starting material or other volatile species as detected by GC/MS.

Gas-phase products are shown in Tables 1 (hydrazines and diazenes) and 2 (single triazine rings). The major decomposition gas observed was nitrogen. A review of the decomposition gases of compounds lacking nitrogen-containing substituents (**A1**, **H1**, **A2**, **H2**) clearly indicates that nitrogen gas is derived from the hydrazo or azo linkage. In the absence of nitrogen-containing substitutents, the diazenes formed about 0.7–0.8 mol N_2 per mole of compound, whereas the analogous hydrazine compounds produced 0.5–0.6 mol N_2 per mole. These values are substantially less than the 1 mol of nitrogen that could be potentially formed from the linkage. The same trend was observed in the thermolysis of azobenzene, which formed 0.47 mol N_2 per mole of compound and hydroazobenzene, which produced 0.26 nitrogen per mole. Presumably, the hydroazo linkage diverts more nitrogen to ammonia production than the azo linkage. Production of nitrogen from the azo linkage is likely to proceed by a free-radical mechanism. A number of studies have examined the decomposition of azoalkanes (R_1-N=N-R_2) [34,35] and found that the symmetry around the azo bond determines the mechanism by which nitrogen is lost. Unsymmetrical bonds favor a two-step, radical loss, whereas symmetrical compounds tend to lose nitrogen in a concerted homolysis; but both mechanisms appear to occur simultaneously [34].

Nitrogen-containing ring substituents produced nitrogen and ammonia gas. Substitution of the triazine ring with amine groups did not dramatically increase nitrogen production, but substitution with hydrazino or azido groups did. Azides are known to thermally decompose to 1 mol of nitrogen and a terminal nitrene (-N::) under some conditions. The latter can rearrange to final products that may or may not include release of the third nitrogen atom [36]. The 1,5-dipolar cyclization of azides to tetrazoles is not stable on the triazine species and does not appear to be influential in the decomposition [37,38]. Instead, triazidotriazine decomposes to release about 4.5 mol of gas; this is 1.5 mol (all three nitrogens) from each azido group.

Decomposition gases resulting from destruction of the actual triazine ring were minor. Ammonia was observed when

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hydrazine was one of the triazine ring substituents. Stoichiometry is such that 1 mol of $NHNH_2$ pendant to the ring would be capable of forming 0.5 mol of N_2 and 1.0 mol NH_3. In the series melamine, diamino hydrazino triazine, dihydrazino amino triazine, and trihydrazino triazine, it was found that each successive hydrazine added about 0.5 mol of nitrogen to the decomposition gases. In similar fashion, **H-6** and **H-7** gave about 1.5 and 2.5 mol of nitrogen corresponding to two and four hydrazino substituents plus a hydrazo linkage, respectively. Increasing ammonia release was detected with increasing hydrazino substituents. However, the chromatographic peak of ammonia was not sufficiently separated from that of water nor did we know the specific response of ammonia; therefore, the quantitation shown in Table 3 is only qualitative.

Carbon-containing thermolysis products were produced in minor amounts, unless the triazine ring possessed a methoxy substituent. Carbonaceous decomposition products were identified as carbon monoxide, methane, methanol, and CO_2. Triazine rings with no methoxy substituents produced, at most, 0.2 mol CO_2 per mole of compound, indicative of only minor ring decomposition. Very small amounts of water, contained on the glass or present as a hydrate, are possible sources of oxygen, and sources of carbon from trapped solvents or reagents are expected to be very low.

Because it was difficult to account for the amount of hydrogen observed in the decomposition products, it was thought that hydration of the crystals or the glassware might have been involved. For that reason several compounds were mulled with 20 wt% water and heated as wetted mixes. Ratios of the decomposition products remained unchanged, though it might be expected that excess water vapor would favor ammonia production (although now chromatographically hidden under a substantial water peak).

Thermal stability screening compared DSC scans collected at 20°C/min (Tables 1 and 2). Some of the scans were difficult to interpret because there were no clear peaks or valleys but rather very low thermal events expressed as wavy baselines. As will be discussed below, we did not think this was a problem

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Table 3

Condensed phase decomposition products found gas chromatography

ID	Linkage or R_1	R_2	R_3	Solvent	Retention	Major mass spectrum fragments m/z
Benzonitrile Capture Products of Amino/Hydrazino Triazines						
Dihydrazino methoxy	-$NHNH_2$	-$NHNH_2$	-OMe	Ph-CN	16.5	187 174 144 103 76 51 43 36 28
H-4	-NHNH-		-NH_2	-OMe	Ph-CN	16.5	187 174 144 103 76 51 43 36 28
Hydrazino diamino	-$NHNH_2$	-NH_2	-NH_2	Ph-CN	16.5	187 144 103 83 76 68 51 43 36 28
Dihydrazino amino	-NH_2	-$NHNH_2$	-$NHNH_2$	Ph-CN	16.5	187 144 103 76 44 36 28
H-6	-NHNH-	-NH_2	-$NHNH_2$	Ph-CN	16.5	187 144 129 103 76 51 43 36 28
Dihydrazino amino	-$NHNH_2$	-$NHNH_2$	-OMe	Ph-CN	16.7	215 201 187 172 103 83 77 69 57 51 44 36 28
H-4	-NHNH-	-NH_2	-OMe	Ph-CN	16.7	215 201 187 172 103 83 77 69 57 51 44 36
Dihydrazino amino	-NH_2	-$NHNH_2$	-$NHNH_2$	Ph-CN	17	233 187 130 103 76 51 44 36 28
H-6	-NHNH-	-NH_2	-$NHNH_2$	Ph-CN	17	233 187 130 103 76 51 44 36 28
Dihydrazino methoxy	-$NHNH_2$	-$NHNH_2$	-OMe	Ph-CN	17.7	235 187 132 117 103 89 77 63 51 44 36 28
H-4	-NHNH-	-NH_2	-OMe	Ph-CN	17.7	235 187 132 117 103 89 77 63 51 44 36 28
Dihydrazino methoxy	-$NHNH_2$	-$NHNH_2$	-OMe	Ph-CN	19.4	248 235 144 129 103 76 51 43 36 28
H-4	-NHNH-	-NH_2	-OMe	Ph-CN	19.4	248 235 144 129 103 76 51 43 36 28
Hydrazino diamino	-$NHNH_2$	-NH_2	-NH_2	Ph-CN	19.4	248 187 144 103 76 51 44 36 28
Dihydrazino amino	-NH_2	-$NHNH_2$	-$NHNH_2$	Ph-CN	19.4	248 144 129 103 76 51 43 36 28
H-6	-NHNH-	-NH_2	-$NHNH_2$	Ph-CN	19.4	248 205 187 180 144 103 76 51 43 36 28
Dimethoxy Triazine Decomposition Products (Solvent Independent)						
Hydrazino dimethoxy	-$NHNH_2$	-OMe	-OMe	Cyclohexanol	9.4	143 128 85 82 70 67 58 43 36 32 28
Hydrazino dimethoxy	-$NHNH_2$	-OMe	-OMe	Ph-CN	9.4	

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H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	9.4																			
A-1	-N = N-		-OMe	-OMe	Ph-CN	9.4																			
H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	12.3					171	157	143	128	113	100	85	76	70	58	54	44	40	36	28
A-1	-N=N-		-OMe	-OMe	Ph-CN	12.3						157		128	113	100		85		70	58	44			28
H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	12.8							142	127	112			84		71	55	43		38	27
A-1	-N = N-		-OMe	-OMe	Ph-CN	12.7					171	157	142	128	113	103		84		71	58	43	36	32	28
H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	13.3					170	157	142	128				82		70	57	44		36	28
A-1	-N=N-		-OMe	-OMe	Ph-CN	13.0					170		142	128	113	103		84		69	57		42	36	28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Cyclohexanol	13.1					170	157	142					82	76	69	57	44			28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Ph-CN	13.0					170	157	142	128	113	103		84		69	57		42	32	28
Hydrazino dimethoxy		$-NHNH_2$	-OMe	-OMe	Cyclohexanol	15.4						158						82	73	67	58	54	41	36	28
H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	15.4						158						82		67	58		41		
A-1	-N = N-		-NH2	-OMe	Cyclohexanol	15.4						158						82	73	67	57	44		36	28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Cyclohexanol	16.3					170	157	141	126	113	103	96	83		69	56	44			28
H-1	-NHNH-		-OMe	-OMe	Cyclohexanol	16.4	224	210	196	182	170	157	141	125	113		97	83		69	56		42	36	30
A-1	-N = N-		-OMe	-OMe	Ph-CN	16.4		210	196	182	170	153	141	125	113		97	82		69	56		42	36	28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Ph-CN	16.4					170	157	141		113	103	96	83		69	56				
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Cyclohexanol	16.7		215	201	187	170	157	141	131	113	104	96	83	77	69	57	51	43	36	28
Hydrazino dimethoxy		$-NHNH_2$	-OMe	-OMe	Ph-CN	16.7		215	201	186	172			131		103		83	76	69	57		43	36	28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Ph-CN	16.7		215	201	187	172	157	141	129	113	104	96	83	77	69	57	50	43		28
Amino dimethoxy		$-NH_2$	-OMe	-OMe	Ph-CN	17	229	215	201	186	170	159	145	129	113	104	96	83	77	69	57	50	43	36	28
-Cyclohexane reaction product 1						10.1						99	82	79	71	67	62	57	54	44	41	39	36	32	28
-Cyclohexane reaction product 2						10.6						99	82	76	71	67		57	55	44	41	39	36	32	28
-1,3,5-trimethyl-1,3,5-triazinane-2,4,6-trione (NIST)						11.5					171		143		113			85		70	58		42		28

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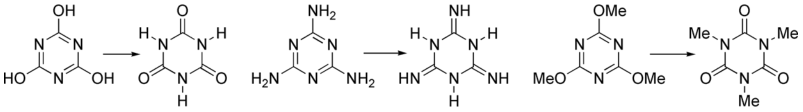
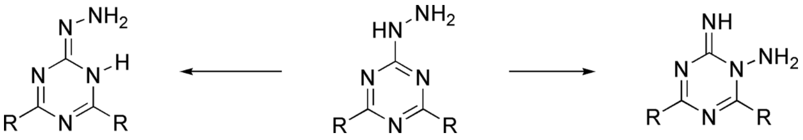
with our technique or instrumentation but rather an artifact resulting from compounds that exhibit endothermic events (melting, phase change, rearrangement), which partially or completely overlapped with exothermic decompositions. In some cases, these endo- and exotherms are very pronounced. Seven of the two dozen compounds screened exhibited no exotherm in the region examined (50–500°C). The compounds showing this exceptional stability were symmetrically substituted triazines (cyanuric acid, cyanuric chloride, and melamine), which have extremely high melting points, and the linked-triazines where the only substituents were chlorine or amine (**A/H-2**, **A/H-3**, **A/H-5**). As a general rule possessing a high melting point makes a compound less subject to thermal decomposition; thus, the stability of cyanuric acid and melamine is reasonable. Among the multi-ring compounds, high stability is only found with two substituents, which have few modes of reactivity available to them.

The importance of the substituents on the triazine ring to thermal stability is evident. Compounds with the same substituents exhibited similar thermal stabilities, regardless of whether they were single-ring triazines or the linked analogs. The least stable compounds were those containing two azides (**A-9**, **H-9**, triazidotriazine) or two methoxy (**A-1**, **H-1**, amino dimethoxytriazine) substituents per triazine; they exhibited an exotherm in the 220–230°C range. Compounds with only one azido substituent per ring (**A-8**, **H-8**) produced an exotherm somewhat higher (~240°C; Trimethoxytriazine appeared an exception with an exotherm around 260°C.)

The observed DSC traces were diverse. A few were a single sharp exotherm; a few exhibited an endotherm greatly separated from an exotherm; some showed an endotherm immediately followed by an exotherm; some showed only one or several endotherms; and a few yielded broad unformed peaks and valleys. As was mentioned above, we believe that these are due to an endothermic event occurring at close temperature, before, during, or after an exothermic event. The most typical of these is the often observed melt-with-decomposition. However, an endotherm can indicate a change



Scheme 5. The rearrangement of cyanuric acid, melamine, and trimethoxy triazine.



Scheme 6. Two possible rearrangement pathways for hydrazine substituents.

in polymorph or, in the case of the methoxy-substituted compound, a rearrangement.

H-1 and amino dimethoxy trazine have similar melting points only slightly lower than **A-1**. Observation of their melting revealed that the melt began with the formation of a clear, colorless liquid followed by a small amount bubbling and, as heating continued, a sudden conversion of the liquid to an opaque solid. This is postulated to be a high melting rearrangement product. **A-1** melted with pronounced decomposition suggesting elimination of the nitrogen linkage; the compound did not re-form a solid. Owing to the methyl rearrangement as described above, only small amounts of CO, CO_2, or methane/methanol were detected. Analogous to the methoxy-rearrangement is that of amino or hydroxyl groups on triazine rings (Scheme 5). A similar reaction with the hydrazine substituent has not been postulated, but that substitution could undergo more than one type of rearrangement (Scheme 6).

Conclusions

Among the triazine compounds examined, it appears that their thermal stability is entirely dependent upon their exo-ring substitution. Data suggest that the triazine ring was stable for

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up to an hour at 550°C. The linkage between two triazine rings did not appear to alter the decomposition of substituents or act as a trigger mechanism for the decomposition of the triazine ring. Even in the azo compounds, breakage of the linkage, evidenced by the evolution of nitrogen, did not produce large quantities of carbonaceous gas. Of course, it is likely that cleavage of the ring did not completely devolve it into simple gases but resulted in C=N polymers and rings as amorphous, insoluble residue. With the exception of the azido-substituted triazine rings, the compounds studied had high thermal stability. The *s*-triazine backbone appears to offer thermal stability not found in other heterocycles; however, further research is necessary before conclusions as to their usefulness as energetic materials can be made.

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