

Anal. Calcd for $C_6H_{14}S_2$: C, 47.94; H, 9.39; S, 42.67; SH, 21.33. Found: C, 47.95; H, 9.3; S, 39.4; SH, 20.5.

Treatment of Ethylenediamine with Ammonium Bisulfide.—The general procedure used with 1-amino-2-propanethiol was followed. Heating 30 g of ethylenediamine, 80 g of ammonia, and 203 g of hydrogen sulfide in 600 ml of water led to no discernible formation of 1,2-ethanedithiol.

Treatment of 3-Amino-1-propanethiol with Ammonium Bisulfide.—The general procedure was followed. Heating 49 g of 3-amino-1-propanethiol, 80 g of ammonia, and 184 g of hydrogen sulfide in 600 ml of water yielded only some black polymeric material. Extraction with ether and inspection of both the extract and aqueous phases by gas-liquid partition chromatography indicated that neither 1,3-propanedithiol nor trimethylene sulfide had been formed.

Differential Thermal Analysis of Nitramines, Amine Salts, and Guanidine Derivatives

YVON P. CARIGNAN AND DANIEL R. SATRIANA

Propellant Laboratory, FRL Picatinny Arsenal, Dover, New Jersey

Received June 23, 1966

A study of the thermal stability of a number of nitramines, amine nitrate salts, and guanidine derivatives by means of differential thermal analysis is presented. The position of the exotherms on the average is at about 260° for both cyclic nitramines and amine nitrate salts. In the open-chain nitramines the decomposition exotherms cover a very broad temperature range and the position of the peak maxima is apparently dictated by the electronegativity of the groups bonded to the amino nitrogens. In the case of the guanidine derivatives salts the decomposition exotherms would seem to depend on both the cation and anion structures and are possibly related to the hydrolysis constants of the salts.

The technique of differential thermal analysis (DTA) has aroused widespread interest for the study of the thermal behavior of numerous organic and polymeric compounds. The simplicity of manipulation and the small amounts of material required render this technique extremely valuable. However, as can be judged by the paucity of published data its potential value in the field of propellants had not been recognized until a few years ago.¹ This is particularly true of compounds of military interest such as nitramines, amine nitrate salts, and guanidine derivatives. Only a few of the latter have to this date been reported.² It is not surprising then that no serious efforts have as yet been made toward establishing some possible correlation between profiles of structural features and thermograms. Such an attempt based on the results obtained from 40 compounds is presented in this paper. These include cyclic and acyclic nitramines, their corresponding salts, and guanidine derivatives. Owing to the complex shape of many thermograms only the position of the exotherm maxima is discussed in relation to the structure of the compounds.

Results and Discussion

Cyclic Nitramines.—As shown in Table I, of the ten cyclic nitramines studied three boiled without decomposition (thermograms 1, 2, and 3). All the other nitramines gave exotherms, the average position of the maxima being at 265°. Throughout this series the exotherm maxima cover a rather broad temperature range (from 240 to 285°) and no clear relationship between structure and the decomposition temperature could be detected. In four of these nitramines (thermograms 6, 7, 8, and 10) it was observed that decomposition occurs near the melting point. With β -HMX (thermogram 10) an endotherm was ob-

served at 185° and has been assigned to the crystal-phase transition from the β form to the metastable δ form in agreement with previous results obtained at other laboratories.^{3,4} This assignment explains satisfactorily the behavior of the endotherm upon repeated heating of the sample to 200°. While immediate reheating results in the disappearance of the endotherm, reheating after a sufficiently long pause at room temperature leaves it unaffected.

Open-Chain Nitramines.—The positions of the exotherm maxima for this series of compounds are given in Table II. It is evident that the type of substitution on the amino nitrogen has a drastic influence on the thermal stability of these compounds. There is a strong indication that a direct relationship might exist between the electronic configuration of the nitramine function and its thermal stability. Replacement of the hydrogen atoms by electron-donating groups as in NN'-dinitro-NN'-dimethyl-1,2-diaminoethane (thermogram 14) shifts the exotherm to higher temperatures while the reverse is observed with electron-withdrawing groups such as carboxyethyl and acetyl (thermograms 15 and 16). Comparison of thermograms 14 and 17 in the open-chain series with those of the cyclic nitramines leads to the suggestion that whether the nitramine function is part of a ring or an open-chain structure apparently has very little bearing on its thermal stability.

In the open-chain series only two compounds (thermograms 12 and 13) incorporate into their structure a primary nitramino group and both compounds are characterized by a relatively low temperature exotherm (202 and 210°). Furthermore, the diammonium and guanidinium salts of the primary nitramine, NN'-dinitro-1,2-diaminoethane (thermograms 26 and 40), have exotherm maxima very close to that of the parent nitramine (191 and 215°). This raises the question as to whether the presence of the tautomeric *aci* form as




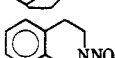



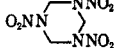
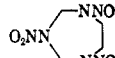
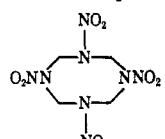
(1) P. G. Rivette and E. D. Besser, "Differential Thermal Analysis as a Research Tool in Characterizing New Propulsion Systems," NAVWEPS Report 7769, U. S. Naval Ordnance Test Station, China Lake, Calif., Oct 1961.

(2) M. I. Fauth, *Anal. Chem.*, **32**, 6, 655 (1960).

(3) Quarterly Progress Report No. 2, Walter C. McCrone Associates, Contract No. NOrd 18840, April 1962.

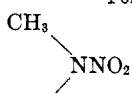
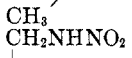

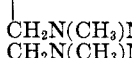
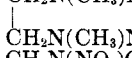
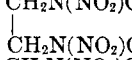
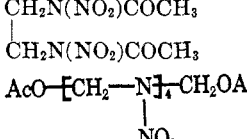
(4) Los Alamos Scientific Laboratory Report LAMS-2652, Contract W-7405-Eng., May 1962.

TABLE I
THERMAL PROPERTIES OF CYCLIC NITRAMINES

Thermogram	Nomenclature	Formula	Exotherm max, °C
1	N-Nitroazacyclohexane		None ^a
2	N-Nitroazacycloheptane		None ^a
3	3-Nitro-3-azabicyclo[3.2.2]nonane		None ^a
4	1-Nitro-3,4-benzo-1-azacyclohexane		276
5	1,3-Dinitro-1,3-diazacyclopentane		246
6	1,3-Dinitro-2-oxo-1,3-diazacyclopentane		238 ^b
7	1,4-Dinitro-1,4-diazacyclohexane		285
8	1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)		250
9	1,3,5-Trinitro-1,3,5-triazacycloheptane		281
10	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)		279 ^b

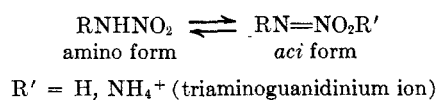
^a Boiled without decomposition. ^b Violent decomposition.

TABLE II
THERMAL PROPERTIES OF OPEN-CHAIN NITRAMINES

Thermogram	Nomenclature	Formula	Exotherm max, °C
11	N-Nitrodimethylamine		None
12	NN'-Dinitro-1,2-diaminoethane		202 ^a
13	NN'-Dinitro-N-methyl-1,2-diaminoethane		210 ^a
14	NN'-Dinitro-NN'-dimethyl-1,2-diaminoethane		285
15	NN'-Dinitro-NN'-dicarboxyethyl-1,2-diaminoethane		216
16	NN'-Dinitro-NN'-diacetyl-1,2-diaminoethane		142 ^a
17	2,4,6,8-Tetranitro-1,9-diacetoxy-2,4,6,8-tetrazanonane		260

^a Violent decomposition.

shown below may not be the common cause for the low thermal stability of these four compounds. The exist-



ence of the *aci* form of primary nitramines has been the subject of controversy for many years⁵ and most recent results support the amino structure at the exclu-

sion of the *aci* structure.⁶⁻⁸ However, small equilibrium concentrations of the *aci* compound could have escaped detection by the technique used in these structural studies, *i.e.*, infrared and X-ray analysis. Furthermore, if the equilibrium was to shift to the right under heating, it is conceivable that at the observed decomposition point the concentration of the *aci* form may be high enough to initiate the decomposition process.

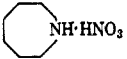
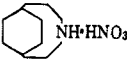
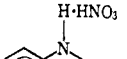
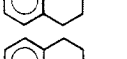
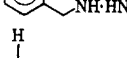
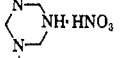
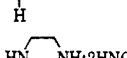
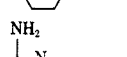
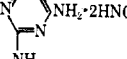
(6) M. Davies and N. Jonathan, *Trans. Faraday Soc.*, **54**, 469 (1958).

(7) C. A. Beevers and A. F. Trotman-Dickenson, *Acta Cryst.* **10**, 34 (1957).

(8) F. J. Llewellyn and F. E. Whitmore, *J. Chem. Soc.*, 1316 (1948).

(5) H. A. Lambertson, *Quart. Rev. (London)*, **5**, 75 (1951).

TABLE III
 THERMAL PROPERTIES OF AMINE SALTS

Thermogram	Nomenclature	Formula	Exotherm max, °C
18	Azacycloheptane nitrate		292
19	3-Azabicyclo[3.2.2]nonane nitrate		258 ^a
20	2,3-Benzo-1-azacyclohexane nitrate		236 ^a
21	3,4-Benzo-1-azacyclohexane nitrate		268 ^a
22	1,3,5-Triazacyclohexane nitrate		213
23	1,4-Diazacyclohexane dinitrate		267 and 304
24	2,4,6-Triamino-1,3,5-triazine dinitrate		337
25	1,3,6,8-Tetraazatricyclo[6.2.1.1 ^{3,6}]dodecane tetranitrate		260 ^a
26	Diammonium-NN'-dinitro-1,2-ethanediamine salt		191 ^a

^a Violent decomposition.

Amine Salts.—As shown in Table III the range of exotherm maxima for the eight nitrate salts is rather large (213 to 337°). However, the two extreme cases (thermograms 22 and 24) are not structurally related to the other salts. For example, both contain free amine groups in the presence of ammonium cations. In addition, compound 24 has some degree of aromaticity and the resonance stabilization of the ring would be expected to have a strong effect on the stability of this salt. Consequently, omitting these two cases it is found that the other salts yield an average exotherm maximum of 263° which is comparable to the average found for the cyclic nitramines. This correspondence in the decomposition temperature of nitramines and nitrate salts may not be purely coincidental. It may, for example, reveal that upon heating the nitrate salts rearrange to the corresponding nitramines with the loss of 1 mole of water. Certainly this hypothesis should be examined further because of potential application in synthesis and in a better understanding of the thermal behavior of nitrate salts in general.

Guanidine Derivatives.—The guanidine derivatives studied by differential thermal analysis are given in Table IV where the data have been grouped on the basis of the anion structure. There are apparently some interesting relationships despite the fact that the list of compounds is far from being complete. From these data tentative assignments for the exotherm peaks have been tabulated in Table V. If these assignments are correct they lead to the following order of thermal stability in respect to the anions: $\text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^- > \text{picrate}$. It is interesting to note that this order of ther-

 TABLE IV
 THERMAL PROPERTIES OF SALTS OF GUANIDINE DERIVATIVES

Thermogram	Nomenclature	Exotherm max, °C
27	Nitroguanidine	250
28	Guanidinium nitrate	270 and 307
29	Aminoguanidinium nitrate	250 and 290
30	Diaminoguanidinium nitrate	260 ^a
31	Triaminoguanidinium nitrate	230 ^a
32	Guanidinium perchlorate	317 and 350 ^a
33	Triaminoguanidinium perchlorate	243 and 317 ^a
34	Aminoguanidinium picrate	235 and 275
35	Triaminoguanidinium picrate	210 and 215
36	Aminoguanidinium chloride	275 and 310
37	Triaminoguanidinium chloride	242
38	Triaminoguanidinium sulfate	185
39	Aminoguanidinium bicarbonate	...
40	Triaminoguanidinium-NN'-dinitro-1,2-ethanediamine salt	215

^a Violent decomposition.

mal stability is reminiscent of the order of acidity or extent of ionization of the conjugate acids: $\text{HClO}_4 > \text{HCl} > \text{HNO}_3 > \text{picric acid}$.⁹ According to Table V it is also observed that the thermal stability of the guanidine derivative salts decreases with respect to the cation in the following order: guanidinium > aminoguanidinium > diaminoguanidinium > triaminoguanidinium. The possibility that this order might be related to the dissociation constant for the bases or the hydrolysis constant of the salts was briefly explored by

(9) T. Moeller "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, pp 314, 316.

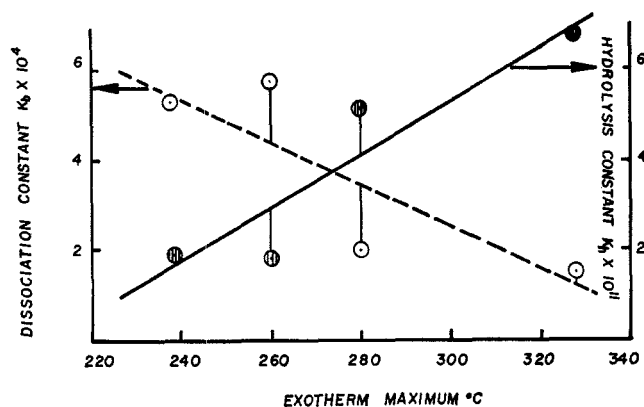


Figure 1.—Relationship between K_b or K_h with the exotherm maxima in the nitrate salts of guanidine derivatives.

TABLE V
TENTATIVE ASSIGNMENTS OF EXOTHERMS OF
GUANIDINE DERIVATIVES^a

Thermogram	Exotherm max, °C							Chloride
	G	AG	DAG	TAG	NO ₂	HClO ₄	Picrate	
28	307				270			
29		290			250			
30			260		260			
31				230	250			
32	350				275	317		
33				243		317		
34		275					235	
35							215	
36		275						310
37				242				
Av	328	280	260	238	261	317	225	310

^a G = guanidinium, AG = aminoguanidinium, DAG = diaminoguanidinium, and TAG = triaminoguanidinium.

measuring the pH values of the nitrate salts of the guanidine derivatives in 0.1 M aqueous solutions. The calculated values for these constants from known relations are given in Table VI. A plot of these values *vs.*

TABLE VI
DISSOCIATION AND HYDROLYSIS CONSTANTS OF NITRATE SALTS
OF GUANIDINE DERIVATIVES

Nomenclature	pH ^a	K_b	K_h
Guanidinium nitrate	5.58	1.51×10^{-4}	6.75×10^{-11}
Aminoguanidinium nitrate	5.64	1.99×10^{-4}	5.13×10^{-11}
Diaminoguanidinium nitrate	5.87	5.74×10^{-4}	1.78×10^{-11}
Triaminoguanidinium nitrate	5.85	5.23×10^{-4}	1.95×10^{-11}

^a pH values were determined in 0.1 M solutions of the salt in water

$$\text{pH} = 0.5\text{p}K_w - 0.5\text{p}K_b - 0.5 \log c$$

$$K_h = K_w/K_b$$

where K_w = ionic product of water 1.02×10^{-14} at 25°, K_b = dissociation constant of the conjugate base, K_h = hydrolysis constant of the salt, and c = concentration of the salt in aqueous solution.

the decomposition exotherms yields the relationship shown in Figure 1. Notwithstanding the wide scattering of the experimental points along the least-square line, it is fairly well indicated that the exotherm maxima are shifted to higher temperatures with an increase in the magnitude of the hydrolysis constants of the salts.

Conclusion

Evidently the limited data presented do not permit sweeping generalizations, but the results strongly indicate that structural features have a controlling in-

fluence on the thermal stability of these molecules. It would thus seem justified to extend this work to include other families of compounds in order to establish on a sound basis of quantitative relationship between the structure of a molecule and its thermal behavior. The proposition that the low stability of primary nitramines may be due to the existence of the *aci* tautomer deserves closer examination. No doubt infrared and/or proton magnetic resonance spectroscopy would be the techniques of choice to test the validity of this hypothesis. Exploratory work has already been conducted in this direction and infrared spectra have been obtained at this laboratory on the three nitramines, NN'-dinitro-1,2-diaminoethane, and both the monomethyl and dimethyl derivatives. The complexity of the spectra have, however, made the analysis very difficult. Furthermore for the spectroscopic study to be of significant value it will have to be conducted at temperatures close to the decomposition point. This is presently being investigated and the results will be reported at a later date.

Experimental Section

The samples, either as finely divided solids or as liquids, were introduced in a 2-mm-diameter capillary tube to a depth of 3 mm and thermograms were obtained with a Du Pont 900 differential thermal analyzer. A chromel-alumel thermocouple wire was inserted in the capillary tube such that the junction was maintained in intimate contact with the sample. In the reference capillary tube, fine glass beads were used as inert material. By means of the temperature programmer the rate of heating was maintained at 20°/min. All runs were conducted while keeping the samples under an atmosphere of nitrogen.

Materials.—1,3,5-Trinitro-1,3,5-triazacyclohexane (thermogram 8, RDX) was synthesized by the method of Bachmann,¹⁰ mp 201–203°.

1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (thermogram 10, HMX) was synthesized according to known procedure,¹¹ mp 276–278°.

N-Nitroazacyclohexane (thermogram 1) was synthesized by the method of Wright,¹² bp 74–76° (2.0 mm), n_D^{20} 1.4940. *Anal.* Calcd for C₅H₁₀N₂O₂: nitro N, 10.76. Found: nitro N, 10.76.

N-Nitroazacycloheptane (thermogram 2) was synthesized by the method of Wright,¹² bp 85–87° (2.0 mm), n_D^{20} 1.5045. *Anal.* Calcd for C₆H₁₂N₂O₂: nitro N, 9.72. Found: nitro N, 9.71.

1,4-Dinitro-1,4-diazacyclohexane (thermogram 7) was synthesized by the method of Wright,¹² mp 214–215°. *Anal.* Calcd for C₄H₈N₄O₄: nitro N, 15.90. Found: nitro N, 15.97.

1-Nitro-3,4-benzo-1-azacyclohexane (thermogram 4) was synthesized by the method of Wright,¹² mp 60–61°. *Anal.* Calcd for C₉H₁₀N₂O₂: nitro N, 7.87. Found: nitro N, 7.84.

3-Nitro-3-azabicyclo[3.2.2]nonane (thermogram 3) was synthesized by the method of Wright,¹² mp 110–111°. *Anal.* Calcd for C₈H₁₄N₂O₂: nitro N, 8.23. Found: nitro N, 8.26.

1,3,5-Trinitro-1,3,5-triazacycloheptane (thermogram 9) was synthesized from N,N'-dinitro-1,2-diaminoethane by the method of Wright,¹³ mp 167–168°. *Anal.* Calcd for C₄H₈N₆O₆: C, 20.34; H, 3.39; N, 35.57. Found: C, 20.86; H, 2.92; N, 35.35.

1,3-Dinitro-2-oxo-1,3-diazacyclopentane (thermogram 6) was prepared by nitration of 2-oxo-1,3-diazacyclopentane (I) with 90% nitric acid and acetic anhydride, mp 219–220°. *Anal.* Calcd for C₄H₆N₄O₅: C, 20.45; H, 2.26; N, 31.81. Found: C, 21.16; H, 2.80; N, 31.50. The intermediate I was synthesized by the method of Bachman.¹⁴

(10) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **71**, 1842 (1949).

(11) T. C. Castorina, F. S. Holahan, R. J. Graybush, J. V. R. Kaufman, and S. Helf, *ibid.*, **82**, 1617 (1960).

(12) W. D. Chute, K. G. Herring, L. E. Toombs, and G. F. Wright, *Can. J. Res.*, **26B**, 89 (1948).

(13) G. S. Myers and G. F. Wright, *ibid.*, **27B**, 489 (1949).

(14) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and C. E. Maxwell, *J. Am. Chem. Soc.*, **72**, 3132 (1950).

1,3-Dinitro-1,3-diazacyclopentane (thermogram 5) was synthesized from N,N'-dinitro-1,2-diaminoethane by the method of Goodman,¹⁵ mp 134–134.5°. *Anal.* Calcd for C₅H₈N₄O₄: C, 22.23; H, 3.70; N, 34.56. Found: C, 22.27; H, 4.07; N, 34.80.

N-Nitrodimethylamine (thermogram 11) was purchased from K & K Laboratories, Inc., Plainview, N. Y., and was used as received, mp 56–57°.

N,N'-Dinitro-N,N'-dicarboxyethyl-1,2-diaminoethane (thermogram 15) was prepared from ethylenediamine according to the procedure of Bachman.¹⁴ Recrystallized from absolute alcohol, it showed mp 82–82.5°.

N,N'-Dinitro-1,2-diaminoethane (thermogram 12) was prepared from N,N'-dinitro-N,N'-dicarboxyethyl-1,2-diaminoethane according to the procedure of Bachman,¹⁴ mp 175–176°.

N,N'-Dinitro-N,N'-diacetyl-1,2-diaminoethane (thermogram 16) was prepared by treating N,N'-dinitro-1,2-diaminoethane with acetic anhydride for 6 hr at 65°. Recrystallized in a mixture of 50:50 (v/v) acetone-petroleum ether (bp 60–70°) gave mp 133–134°. *Anal.* Calcd for C₈H₁₀N₄O₆: C, 30.77; H, 4.27; N, 23.93. Found: C, 30.92; H, 4.42; N, 24.57.

N,N'-Dinitro-N-methyl-1,2-diaminoethane (thermogram 13) was prepared by methylating the monopotassium salt of N,N'-dinitro-1,2-diaminoethane in aqueous solution with a 50% excess of dimethyl sulfate. After 15 min of reaction, during which the temperature rose spontaneously to 45°, the mixture was cooled and filtered. The crude product was dissolved in an aqueous potassium hydroxide solution to separate the insoluble dimethyl derivative. Acidification of the solution, filtration, and recrystallization from hot water yielded crystals, mp 120–121°. *Anal.* Calcd for C₅H₈N₄O₄: C, 21.95; H, 4.88; N, 34.15. Found: C, 22.48; H, 4.69; N, 34.38.

N,N'-Dinitro-N,N'-dimethyl-1,2-diaminoethane (thermogram 14) was obtained as a by-product in the preparation of the monomethyl derivative. Recrystallization from 50% ethanol gave mp 136–137°. *Anal.* Calcd for C₇H₁₀N₄O₄: C, 26.97; H, 5.62; N, 31.46. Found: C, 26.60; H, 5.48; N, 31.48.

2,4,6,8-Tetranitro-1,9-diacetoxy-2,4,6,8-tetrazanonane (thermogram 17) was synthesized according to the procedure of Bachman.¹⁶ Recrystallization from acetic acid gave mp 186–187°. *Anal.* Calcd for C₉H₁₆N₈O₁₂: C, 25.23; H, 3.74; N, 26.17. Found: C, 25.64; H, 3.85; N, 25.70.

Amine nitrate salts were prepared by treating the corresponding amine with 70% nitric acid at low temperature following the procedure of Wright.¹²

Azacycloheptane nitrate (thermogram 18) had mp 120–123°. *Anal.* Calcd for C₆H₁₁N·HNO₃: nitrate N, 8.64. Found: nitrate N, 8.69.

3-Azabicyclo[3.2.2]nonane nitrate (thermogram 19) had mp 218–221°. *Anal.* Calcd for C₈H₁₅N·HNO₃: nitrate N, 7.44. Found: nitrate N, 7.44.

2,3-Benzo-1-azacyclohexane nitrate (thermogram 20) had mp 125°.

3,4-Benzo-1-azacyclohexane nitrate (thermogram 21) had mp 122–124°. *Anal.* Calcd for C₉H₁₁N·HNO₃: nitrate N, 7.14. Found: nitrate N, 7.11.

1,3,5-Triazacyclohexane nitrate (thermogram 22) had mp 172–175°. *Anal.* Calcd for C₃H₅N₃·HNO₃: nitrate N, 9.33. Found: nitrate N, 9.85.

1,4-Diazacyclohexane dinitrate (thermogram 23) had mp 195–197°. *Anal.* Calcd for C₄H₁₀N₂·2HNO₃: nitrate N, 13.21. Found: nitrate N, 13.33.

2,4,6-Triamino-1,3,5-triazine dinitrate (thermogram 24) had mp 204°.

1,3,6,8-Tetraazatricyclo[6.2.1.1^{3,6}]dodecane tetranitrate (thermogram 25) had mp 185°. *Anal.* Calcd for C₈H₁₆N₄·4HNO₃: nitrate N, 58.88. Found: nitrate N, 59.28.

Diammonium N,N'-dinitro-1,2-ethanediamine salt (thermogram 26) had mp 179–180°. *Anal.* Calcd for C₂H₆O₄N₄·2NH₃: ammonium N, 18.48. Found: ammonium N, 18.21.

The guanidinium salts were prepared by two known procedures: (1) cyanamide and the corresponding ammonium salt according

to Blair's procedure¹⁷ and (2) dicyandiamide and sulfuric acid as described by Davis.¹⁸

Guanidinium nitrate (thermogram 28) had mp 212°.

Guanidinium perchlorate (thermogram 32) had mp 178°.

Aminoguanidinium bicarbonate (thermogram 39) was prepared by treating a cyanamide solution with hydrazine under a current of carbon dioxide as described by Lieber.¹⁹ The other aminoguanidinium salts were prepared from the bicarbonate and the appropriate acid.

Aminoguanidinium picrate (thermogram 34) had mp 185°. *Anal.* Calcd for CH₅N₄·C₆H₃N₃O₇: C, 27.72; H, 2.97; N, 32.34. Found: C, 27.59; H, 2.88; N, 31.42.

Aminoguanidinium nitrate (thermogram 29) had mp 144.5–145.5°.

Aminoguanidinium chloride (thermogram 36) had mp 160–161°.

Diaminoguanidinium nitrate (thermogram 30) was prepared by treating an aqueous solution of barium nitrate with diaminoguanidinium sulfate. After standing overnight the solution was filtered and the filtrate was reduced to a minimum volume in a flash evaporator. Recrystallization from a water-ethanol mixture gave mp 144–145°.

Triaminoguanidinium nitrate (thermogram 31) was prepared according to the following procedure. In a 200-ml, three-necked, round-bottom flask, fitted with a mechanical stirrer, 16.8 g (0.2 mole) of dicyandiamide was added to a solution containing 23.75 g (0.25 mole) of hydrazine nitrate (25% excess) and 35.3 g (0.6 mole) of hydrazine hydrate (85% solution). The mixture was heated at 85–90° by means of an oil bath for 3.5 hr. Then 110 ml of water was added. Heating was continued until the solid dissolved. The solution was quickly transferred to a beaker and chilled in an ice bath. The product was filtered, washed with cold water, and dried in an oven at 100° or in a vacuum desiccator over sulfuric acid. The yield was 29.3 g (87.5%), mp 215–216°. *Anal.* Calcd for CH₅N₆·HNO₃: total N, 58.68. Found: total N, 58.42.

All other triaminoguanidinium salts were prepared from an aqueous solution of the free base by adding the appropriate acid. The triaminoguanidine free base was prepared as follows. To a solution containing 2.4 g of sodium hydroxide dissolved in 30 ml of water was added 10.0 g of triaminoguanidinium nitrate. Solution was effected by mild heating on the steam bath, and 60 ml of dimethylformamide was added to the clear solution. The solution was then rapidly chilled in a Dry Ice-acetone bath with vigorous intermittent shaking until a precipitate was formed. The precipitate was filtered and washed to yield 4.65 g (73.8%) of product, mp 112–120°. *Anal.* Calcd for CH₅N₆: total N, 80.72. Found: total N, 80.55.

Triaminoguanidinium perchlorate (thermogram 33) had mp 134–135°. *Anal.* Calcd for CH₅N₆·HClO₄: Cl, 17.35. Found: Cl, 17.70.

Triaminoguanidinium picrate (thermogram 35) had mp 170–171°. *Anal.* Calcd for CH₅N₆·C₆H₃O₇N₃: C, 25.23; H, 3.30; N, 37.84. Found: C, 25.58; H, 3.56; N, 37.61.

Triaminoguanidinium chloride (thermogram 37) had mp 224–225°. *Anal.* Calcd for CH₅N₆·HCl: total N, 59.79. Found: total N, 60.10.

Triaminoguanidinium sulfate (thermogram 38) had mp 165°. *Anal.* Calcd for CH₅N₆·H₂SO₄: C, 7.84; H, 5.88; N, 54.01; SO₄, 31.37. Found: C, 8.14; H, 6.35; N, 52.82; SO₄, 30.98.

Triaminoguanidinium N,N'-dinitro-1,2-ethanediamine salt (thermogram 40) had mp 191–193°. *Anal.* Calcd for CH₅N₆·C₂H₆O₄N₄: C, 13.41; H, 6.15; N, 62.57. Found: C, 14.60; H, 6.30; N, 62.10.

Nitroguanidine (thermogram 27) was obtained from K & K Laboratories, Inc., Plainview, N. Y., and was used without further purification, mp 56–58°.

Acknowledgments.—The authors are indebted to Dr. H. Matsuguma and Messrs. S. Helf and L. Avrami of the Explosives Laboratory for their guidance in the use of their differential thermal analyzer.

(15) L. Goodman, *J. Am. Chem. Soc.*, **75**, 3019 (1953).

(16) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, and L. B. Scott, *ibid.*, **73**, 2769 (1951).

(17) J. S. Blair and J. M. Braham, *ibid.*, **44**, 2342 (1922).

(18) T. L. Davis, *ibid.*, **43**, 669 (1921).

(19) E. Lieber and G. B. L. Smith, *Chem. Rev.*, **25**, 213 (1939).