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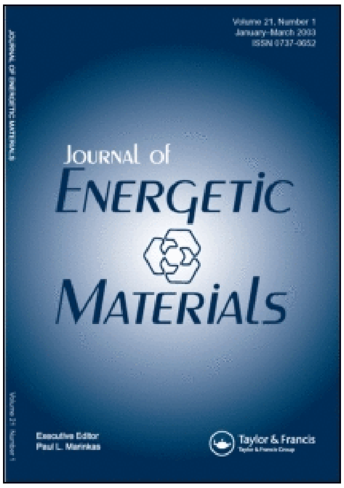

Journal of Energetic Materials

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

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To cite this Article Hiskey, Michael A. , Stinecipher, Mary M. and Brown, James E.(1993) 'Synthesis and initial characterization of some energetic salts of 3,3-dinitroazetidine', Journal of Energetic Materials, 11: 3, 157 — 165

To link to this Article: DOI: 10.1080/07370659308227808

URL: http://dx.doi.org/10.1080/07370659308227808

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SYNTHESIS AND INITIAL CHARACTERIZATION OF SOME ENERGETIC SALTS OF 3,3-DINITROAZETIDINE

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ABSTRACT

Six energetic salts of 3,3-dinitroazetidine (DNAZ) were prepared. Methods of preparation for the nitrate (1), 2,4-dinitroimidazolate (2), 4,4',5,5'-tetranitro-2,2'-biimidazolate (3), dinitramidate (4), 5-nitro-1,2,4-triazol-3-onate (5), and 3,5-dinitro-1,2,4-triazolate (6) are given. Results from initial characterization, small-scale sensitivity tests, heats of formation, density, and ^{13}C-nmr spectra are also reported. DNAZ-nitrate (1) was easily dehydrated to 1,3,3-trinitroazetidine (TNAZ) (7).

INTRODUCTION

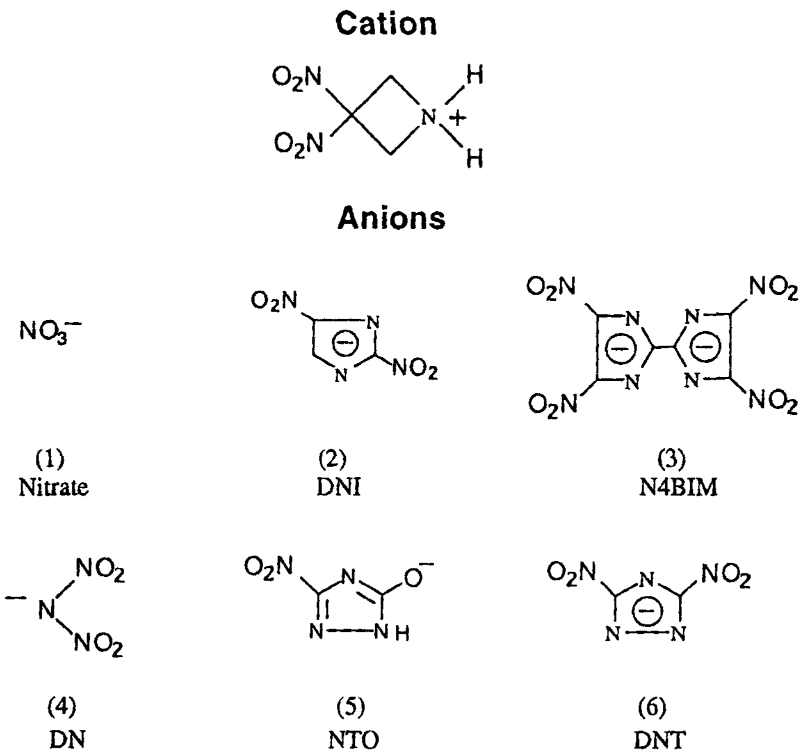
Azetidine-based explosives, such as 1,3,3-trinitroazetidine (TNAZ)[2] (7) are expected to have excellent performance, in part, because of the high strain energy associated with the four-membered ring. We recently reported the preparation of 3,3-dinitroazetidine (DNAZ) from 1-t-butyl-3,3-dinitroazetidine and determined its pK_b as 6.5.[3] The basicity of DNAZ allows the preparation of

Journal of Energetic Materials Vol. 11, 157-166 (1993)
Published in 1993 by Dowden, Brodman & Devine, Inc.

a large variety of salts. Energetic anions are quite common, especially of nitro-substituted 5-membered heterocyclic aromatic rings. Energetic cations, with this high an oxygen balance, are unknown. Thus, the 3,3-dinitroazetidinium cation is useful as an energy-rich substitute for existing cations, such as ammonium, guanidinium, aminoguanidinium, or hydrazinium ions. Here we report the preparation and initial characterization of the following salts of DNAZ shown in FIGURE 1.

FIGURE 1

Anions Used to Form Salts with the New Cation of 3,3-Dinitroazetidine.



RESULTS

The DNAZ salts were prepared by either mixing the free base 3,3-dinitroazetidine with the appropriate acid or by metathesis of 3,3-dinitroazetidinium trifluoromethanesulfonate[3] with the ammonium salt of the acid. All the new salts were subjected to small-scale thermal and sensitivity tests. The tests were performed according to standard procedures[4], and the results are reported in TABLE 1. The compounds are listed according to increasing weight percentage of nitrogen and compared to RDX.

TABLE 1

A Comparison of the DNAZ Salts to RDX in Small-Scale Sensitivity Tests

Name	**Formula**	**N [%]**	**DTA Exotherm [°C]**	**Drop Weight Impact Height Type 12 [cm]**	**Spark Test 3-mil Foil [J]**
DNAZ-Nitrate	$C_3H_6N_4O_7$	26.67	150	32	0.5
DNAZ-DNI	$C_6H_7N_7O_8$	32.14	160	54	0.9
2DNAZ-N4BIM	$C_{12}H_{12}N_{14}O_{16}$	32.25	150	71	1.3
DNAZ-DN	$C_3H_6N_6O_8$	33.08	140	14	1.1
DNAZ-NTO	$C_5H_7N_7O_7$	35.39	160	42	0.6
DNAZ-DNT	$C_5H_6N_8O_8$	36.61	150	37	0.5
RDX	$C_3H_6N_6O_6$	37.84	205	23	0.2

The heats of formation (ΔH_f) of the DNAZ salts were calculated from the heats of combustion measured by burning the compounds in a Parr combustion bomb under 30 atm oxygen pressure. To correct the heat of combustion from nitric acid formation, the bomb washings were titrated with sodium carbonate solution in all runs. The heats of formation of 2DNAZ-N4BIM and DNAZ-DNI had a wide scatter because of combustion problems (TABLE 2). Densities of the DNAZ salts were determined by x-ray crystallography.[5] Densities and heats of formation are listed in TABLE 2.

TABLE 2

Heats of Formation and Densities of DNAZ Salts

Compound	ΔHf (kcal/mol)	Density (g/cm^3)
DNAZ-Nitrate	-64 ± 2	1.764
DNAZ-DNI	-18 ± 12	1.656
2DNAZ-N4BIM	+5 ± 15	1.782
DNAZ-DN	-8 ± 4	1.791
DNAZ-NTO	-48 ± 1	1.757
DNAZ-DNT	+20 ± 2	1.694

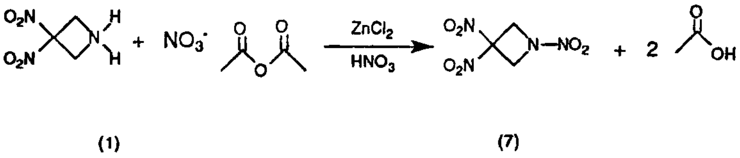
SUMMARY

Six new energetic salts utilizing the novel ion 3,3-dinitroazetidinium have been prepared. We have also prepared eight additional salts, but their properties do not warrant reporting; however, they do illustrate the generality of the preparations. These materials may be useful as propellant ingredients, and sufficient information is given in TABLES 1 and 2 for the appropriate calculations.

An additional use of DNAZ-nitrate (1) is as an alternate route to TNAZ (7). DNAZ-nitrate (1) is dehydrated in excellent yield with acetic anhydride containing catalytic amounts of zinc chloride and nitric acid, SCHEME 1.[6]

SCHEME 1

Dehydration of DNAZ-Nitrate



EXPERIMENTAL

All starting materials were obtained from commercial sources or prepared from the referenced literature. All nmr spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts are relative to internal tetramethylsilane. ^{1}H nmr shifts for the DNAZ cation are given in reference 3. Microanalyses were performed by C.A. Martinez at Los Alamos National Laboratory. All melting points were determined at 2°C/minute with a Mettler FP1 apparatus and are corrected.

3,3-Dinitroazetidinium Nitrate (DNAZ-Nitrate) (1)

Ammonium nitrate (1.50 g, 18.74 mmol) was dissolved in 20 ml of methanol with stirring, and to this was added 3,3-dinitroazetidinium trifluoromethanesulfonate (5.57 g, 18.74 mmol) in 50 ml of methanol. After about 1 minute of stirring, the product precipitated. The suspension was cooled and filtered to yield 2.6 g of product. The filtrate was reduced in volume to yield an additional 1.0 g of product. Total yield 3.60 g (91%), mp 142°C dec. ^{13}C nmr (deuteriomethylsulfoxide) δ 53.3, 107.3. IR (KBr) 3060, 2930, 2660, 2450, 1620, 1430, 1340, 1240, 850, 420 cm^{-1}.

Anal. Calcd for $C_3H_6N_4O_7$: C, 17.15; H, 2.88. Found: C, 17.18; H, 2.96.

3,3-Dinitroazetidinium 2,4-Dinitroimidazolate (DNAZ-DNI) (2)

To a solution of 2,4-dinitroimidazole[7] (1.07 g, 6.77 mmol) in 50 ml of warm acetonitrile was added 3,3-dinitroazetidine (1.0 g, 6.77 mmol). The solution was allowed to cool, and most of the solvent evaporated. The slurry was filtered and dried to yield 1.98 g (95%) of product, mp 151°C dec. ^{13}C nmr (deuteriomethylsulfoxide): δ 53.3, 107.4, 129.6, 146.6, 153.2. IR (KBr) 3150, 3070, 2990, 2900, 2660, 2450, 1590, 1515, 1485, 1310, 1010, 840 cm^{-1}.

Anal. Calcd for $C_6H_7N_7O_8$: C, 23.62; H, 2.31. Found: C, 23.78; H, 2.39.

Di-(3,3-Dinitroazetidinium) 4,4', 5,5'-Tetranitro-2,2'-biimidazolate (2 DNAZ-N4BIM) (3)

To 4,4', 5,5'-tetranitro-2,2'-biimidazole dihydrate[8] (2.0 g, 5.71 mmol) dissolved in 100 ml of warm water was added 3,3-dinitroazetidine (1.68 g, 11.42 mmol) in 5 ml of methanol. A bright yellow precipitate formed immediately, which was filtered and air dried to yield 2.92 g (84%), mp 154°C dec. ^{13}C nmr (deuteriomethylsulfoxide): δ 53.3, 107.5, 140.0, 143.1. IR (KBr) 3200, 3050, 2980, 1580, 1530, 1505, 1470, 1395, 1310, 1225, 845, 810 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}N_{14}O_{16}$: C, 23.69; H, 1.99. Found: C, 23.73; H, 2.07.

3,3-Dinitroazetidinium Dinitramidate (DNAZ-DN) (4)

Ammonium dinitramide[9] (0.25 g, 2.01 mmol) was dissolved in 2 ml of water and loaded on a Dowex 50-W H^+-form water-washed column of approximately 20 ml of volume. The column was eluted with 3 column volumes of water. The solution of dinitramidic acid was neutralized with 3,3-dinitroazetidine (0.29 g, 2.01 mmol) dissolved in 5 ml of methanol. The water was removed by rotary evaporation. The resulting solid was repeatedly recrystallized from ethyl acetate/toluene to yield 0.44 g (86%) of product as a white powder, mp

139°C dec. ^{13}C nmr (deuteriomethylsulfoxide) δ 53.3, 107.2. IR (KBr) 3150, 3060, 2990, 2920, 2640, 2450, 1990 (weak), 1590, 1510, 1430, 1325, 1270, 1180, 1025, 935, 750, 450 cm^{-1}.

Anal. Calcd for $C_3H_6N_6O_8$: C, 14.18; H, 2.38. Found: C, 14.59; H, 2.45.

3,3-Dinitroazetidinium 5-Nitro-1,2,4-triazol-3-onate (DNAZ-NTO) (5)

To 5-nitro-1,2,4-triazol-3-one[10] (0.88 g, 6.76 mmol) in 50 ml of warm methanol was added 3,3-dinitroazetidine (1.0 g, 6.76 mmol). A yellow solid immediately precipitated from solution. The suspension was cooled, and some of the methanol evaporated before filtering and air drying to yield 1.75 g (93%), mp 161°C dec. ^{13}C nmr (deuteriomethylsufoxide): δ 53.8, 111.6, 150.1, 156.2. IR (KBr) 3180, 3060, 2770, 2410, 1650, 1590, 1515, 1380, 1310, 1050, 780 cm^{-1}.

Anal. Calcd for $C_5H_7N_7O_7$: C, 21.67; H, 2.55. Found: C, 21.72; H, 2.64.

3,3-Dinitroazetidinium 3,5-Dinitro-1,2,4-triazolate (DNAZ-DNT) (6)

Ammonium 3,5-dinitro-1,2,4-triazolate[11] (1.0 g, 5.68 mmol) was dissolved in 30 ml of absolute ethanol, and 3,3-dinitroazetidinium trifluoromethanesulfonate (1.69 g, 5.68 mmol) dissolved in 5 ml of absolute ethanol was added with stirring. A precipitate formed and was filtered. The filtrate was reduced in volume, and the precipitate was filtered through the original cake. The cake was washed with cold absolute ethanol and air dried to yield 1.42 g (82%), mp 148°C dec. ^{13}C nmr (deuteriomethylsulfoxide) δ 53.3, 107.2, 162.8. IR (KBr) 3040, 2930, 2660, 2450, 1585, 1550, 1505, 1405, 1370, 1310, 850, 650 cm^{-1}.

Anal. Calcd for $C_5H_6N_8O_8$: C, 19.62; H, 1.98. Found: C, 19.75; H, 2.05.

1,3,3-Trinitroazetidine (TNAZ) (7)

To acetic anhydride (1.50 g, 14.7 mmol) was added 0.030 g of 90% nitric acid and 0.026 g of anhydrous zinc chloride. To this was added DNAZ-nitrate (1) (1.0 g, 4.8 mmol). The very thick slurry was heated to 40°C; at which point, complete solution occurs. The solution was allowed to cool to room temperature, drowned with water, and allowed to crystallize. The product was filtered, washed with water, and dried to yield 0.87 g pure TNAZ (95%). This material was spectrally identical to an authentic sample of TNAZ prepared from the method given in reference 2.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy. The authors are grateful to W. Koppes and A. Stern of the Naval Surface Warfare Center, White Oak, for the expedient preparation of a sample of DNAZ-DN for x-ray analysis, as well as R. Miller of the Office of Naval Research, and R. Gilardi of the Naval Research Laboratory.

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