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ENERGETIC COMPOUNDS FOR USE IN SHAPED-CHARGE, FOLLOW-THROUGH DEVICES

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Six organic compounds (4,5-dihydro-3-nitroisoxazole, 2,2-dinitropropane, 1,1-dinitroethane, 1,3-dinitropropane, nitrocyclopropane, and *trans*-1,2-dinitrocyclopropane) were prepared for detonation testing. Sensitized nitromethane solutions of these compounds were detonated using plastic blocks to observe blast power. The volume of the crater in the observation block was measured: the larger the crater, the more powerful the detonation. A statistical treatment of the results was performed. 1,1-Dinitroethane and *trans*-1,2-dinitrocyclopropane gave the most promising results. 1,3-Dinitropropane was also promising. A synergistic effect was noted between 4,5-dihydro-3-nitroisoxazole and nitromethane. Calorimetry studies were performed on most of the compounds, and the results were compared to the detonation studies. Nitrocyclopropane gave poor results in detonation testing but good results in the calorimetry study. Other calorimetry results agreed with the detonation ones.

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PREFACE

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CONTENTS

FIGURES

TABLES

ENERGETIC COMPOUNDS FOR USE IN SHAPED-CHARGE, FOLLOW-THROUGH DEVICES

1. INTRODUCTION

Six organic compounds (structures **1-6**), shown in Table 1, were selected for synthesis and testing as new explosive materials for use in shaped-charge, follow-through devices. These compounds were selected by the following criteria: (a) theoretical high-energy potential, (b) either liquid or a low-melting solid readily soluble in nitromethane, (c) reasonable synthetic procedures either already available or easily designable based on literature references, and (d) all compounds are members of general classes from which related compounds could be picked for further investigation.

The six compounds selected were synthesized in as large a quantity as practical in an organic chemistry research laboratory. The first five compounds were prepared in 15-50 g quantities. Compound **6**, the most difficult to synthesize, was prepared in a 1 g quantity.

Explosive compositions of candidate compounds were diluted in nitromethane to study their energetic properties. Test detonations were conducted on 25-mL samples, where one-fourth to one-third of the volume was the test compound, and the remainder was nitromethane and a sensitizer, which was required for detonation. Consequently, morpholine, a known nitromethane sensitizer, was added to each candidate explosive composition. Remaining portions of the candidate compounds were combusted in a calorimeter to check the detonation results, and the heat of combustion was measured. Results were referenced to nitromethane for both the detonation and calorimetry studies.

2. SYNTHESIS

All six compounds presented in Table 1 were successfully synthesized. The first five were prepared in 15-30 g quantities. Compound **6**, the most difficult to obtain, was prepared in a 1 g quantity. Solids **2** and **6** were tested for solubility in nitromethane and were soluble in excess of 1 g/4 mL. Structure identification and purity were determined by the usual spectral techniques [i.e., NMR, IR, MS, and TLC (one spot)].

2.1 Synthesis of Compound 1: 4,5-Dihydro-3-nitroisoxazole (DHI).

Compound **1** was prepared by a procedure originally developed by Wade.[1] 1-Bromo-3-chloropropane (157.5 g) was added to a solution of $NaNO_2$ (138 g) and *n*-propyl nitrite[2] (50.3 g) in DMSO (1 L). The resulting mixture was stirred mechanically for 20 hr. During the first hour, the reaction temperature was allowed to rise from 21-40 ^oC but not allowed to exceed 40 ^oC. Intermittent cooling of the reaction flask with an ice-water bath was required to maintain temperature control. (*Caution!* On one duplicate run, the reaction was not cooled sufficiently, and the temperature rose above 50 ^oC. At that point, the reaction rapidly became exothermic and uncontrollable. Reaction contents erupted violently through the condenser.) One hour after this episode, the reaction temperature slowly subsided without further cooling from 40 ^oC to room temperature.

Work-up was accomplished by pouring the reaction mixture into ice water (4 L). Compound **1** was extracted with three 400-mL portions of methylene chloride. The combined extracts were washed with three 1-L portions of water to remove DMSO, were dried over anhydrous Na_2SO_4, and were concentrated at reduced pressure. The concentrate was distilled at reduced pressure, and the fraction (51.8 g, 45% yield) boiling at 78-80 ^oC (0.3 mmHg) was collected as product. Spectra were consistent with published spectra.

2.2 Synthesis of Compound 2: 2,2-Dinitropropane (DNP[1]).

Compound **2** was prepared by Kornblum nitration,[3] a general procedure reported also in the patent literature for synthesis of compound **2**. 2-Nitropropane (8.9 g) was added to a NaOH solution (4.8 g NaOH in 130 mL methanol and 170 mL water). The resultant mixture was stirred until a homogeneous solution was obtained, and this was added dropwise over 30 min to a vigorously stirred mixture containing $K_3Fe(CN)_6$ (163 g), $NaNO_2$ (69 g), water (670 mL), and pentane (1300 mL) kept under argon. Stirring was continued for 60 min. The organic layer was separated, and the aqueous layer was extracted with pentanes (two 500-mL portions). The combined organic layers were washed with water (two 250-mL portions), and dried over anhydrous Na_2SO_4. The concentration provided 8.8 g (66% yield) of slightly impure compound **2,** which was recrystallized from warm pentanes to give 5.9 g of pure compound **2** (mp 50-51 ^oC). The procedure was repeated twice to obtain 16.6 g of compound **2**.

2.3 Synthesis of Compound 3: 1,1-Dinitroethane (DNE).

Compound **3** was prepared by a procedure originally developed by Kaplan and Shechter.[4] Nitroethane (30 g) and $NaNO_2$ (8 g) were added to aqueous NaOH (17 g NaOH in 160 mL water). The resultant mixture was stirred until a homogeneous solution was obtained; this was poured into a stirred cold (0-5 °C) mixture of $AgNO_3$ (141 g), aqueous NaOH (four drops, Ag_2O was present), and diethyl ether. The initial cream-colored solid blackened over a few minutes. The cooling bath was removed, and the mixture was stirred for 30 min. Silver and other solids were filtered off and washed with several portions of dichloromethane. The organic layer and washings were combined and concentrated to give an oily residue. Distillation provided pure compound **3** (25.9 g; 53% yield) boiling at 60-61 °C (6 mmHg) and a forecut containing impure compound **3**.

Alternatively, compound **3** was prepared by Kornblum nitration,[3] a superior procedure not requiring expensive $AgNO_3$ but previously untested for this preparation. Nitroethane (15.5 g) was added to an aqueous NaOH solution (18.8 g NaOH in 200 mL water). The resultant mixture was stirred until a homogenous solution was obtained. This was poured into a second solution containing $K_3Fe(CN)_6$ (165 g) and $NaNO_2$ (74 g) in water (1 L) kept under argon. Stirring was continued for 150 min. Methylene chloride (100 mL) was added, then glacial acetic acid (10 mL) was added, giving off brown fumes. The organic layer was separated, washed with water (50 mL), and dried over anhydrous Na_2SO_4. Distillation provided pure compound **3** (10 mL) boiling at 60-63 °C (6 mmHg).

2.4 Synthesis of Compound 4: 1,3-Dinitropropane (DNP[2]).

Compound **4** was prepared by reacting 1,3-diiodopropane with $AgNO_2$ in ether.[5] A mixture of freshly-prepared $AgNO_2$ (164.3 g) and anhydrous diethyl ether (252 mL) was mechanically stirred and cooled to -1 °C using an ice-salt bath. Distilled 1,3-diiodopropane (127.8 g) was added to the cold stirred mixture dropwise over 1 hr. The cooling bath was allowed to thaw, and stirring was continued at ambient temperature for 24 hr. Ether was added, and the mixture was filtered to remove silver salts, which were washed with two portions of dichloromethane. Solvents were removed at reduced pressure, and the residue was added dropwise to mechanically stirred, cold, concentrated H_2SO_4 (200 mL) to destroy the nitrite ester side product. The reaction temperature was maintained at < 8 °C during the addition. The resulting cold mixture was added to ice-water (500 g); extraction with dichloromethane, water washing, drying with anhydrous Na_2SO_4, and concentration at reduced pressure afforded a crude product. The crude product was twice distilled to provide 18.7 g (32% yield) of pure compound **4** (bp 115-120 °C, 0.1 mmHg). The procedure was repeated to provide another 17 g (30% yield) of compound **4**.

2.5 Synthesis of Compound 5: Nitrocyclopropane (NCP).

Two routes were investigated for preparing nitrocyclopropane (compound **5**). The first route, developed by Kai and co-workers,[6] involved a three-step sequence beginning with 1-bromo-3-chloropropane. First, a solution of 1-bromo-3-chloropropane (280 g, 1.77 mol) in DMSO (700 mL) was prepared and cooled under argon to 16 °C. After 20 min, $NaNO_2$ (106.2 g, 1.53 mol in 10 equal portions) was added while the reaction temperature was kept at 14-16 °C with a cold water cooling bath (only occasional cooling needed). Use of the cooling bath was discontinued, and the temperature was allowed to rise to 30 °C (12 min); whereupon, the reaction was immediately quenched by adding ice-cold water (1 L). The product was extracted with dichloromethane (three 250-mL portions). The combined extracts were washed with water (three 250-mL portions), dried over anhydrous $MgSO_4$, filtered, and concentrated to an oil. Distillation afforded a large forecut of impure starting material followed by 58.8 g (27% yield) of 1-chloro-3-nitropropane (bp 85-95 °C, 18 mmHg), sufficiently pure for the next step.

A mixture of 1-chloro-3-nitropropane (58 g, 0.47 mol), NaI (159.5 g, 1.1 mol), and acetone (460 mL) was refluxed for 43 hr and filtered. The filtrate was concentrated; water (100 mL) and dichloromethane (100 mL) were added to the residue. The layers were separated, and the aqueous layer was extracted with dichloromethane (two 50-mL portions). The organic layers were combined, dried over Na_2SO_4, and concentrated to afford 100.9 g (100% yield) of 1-iodo-3-nitropropane, which was used without further purification in the next step.

A mixture of 1-iodo-3-nitropropane (96 g, 0.45 mol), K_2CO_3 (112 g, 0.8 mol), and benzene (400 mL) was heated under reflux under argon with vigorous stirring for 3 hr. The mixture was cooled and filtered; the solids were washed with benzene (three 60-mL portions). The combined filtrate and washings were concentrated at atmospheric pressure, and the oily residue distilled at reduced pressure to give 9.8 g (25% yield) of nitrocyclopropane (compound **5**) (bp 33-34 °C, 11 mmHg).

The above route to prepare nitrocyclopropane was not entirely satisfactory because of the reduced yield and excessive number of steps. In particular, the first step is not amenable to scale up because of a difficulty in controlling the large exotherm. Thus, we chose to develop a new route to nitrocyclopropane synthesis. Yu and co-workers[7] were able to cyclize a number of 3-nitro alcohols via a Mitsunobu reaction to produce nitrocyclopropanes. However, preparation of the parent compound **5** from 3-nitro-1-propanol was not investigated.

To prepare 3-nitro-1-propanol, the procedures of Jager and co-workers[8] were used. Borane · dimethyl sulfide reduction of commercially available 3-nitropropanoic acid was employed first. Borane · dimethyl sulfide (26.2 mL of a 2 M solution in ether) was added dropwise over 15 min to a stirred solution of 3-nitropropanoic acid (2.53 g, 22 mmol) in ether (60 mL), and the resulting mixture stirred for 2 hr at 20 °C, followed by stirring under reflux for 1 hr. The mixture was cooled to 0-5 °C and methanol (40 mL) was cautiously added to destroy excess borane. The mixture was kept in the freezer overnight and concentrated at reduced pressure later. The residue was dissolved in ether and filtered twice through $NaCO_3$ to give 2 g of 3-nitropropanol as a light-yellow oil suitable for the next step.

For large scale preparations, it was less expensive to prepare 3-nitropropanol from 3-nitropropanal, made from acrolein.[8] Glacial acetic acid (23.9 g) was added dropwise over 1 hr to a vigorously stirred cold (0-5 °C) mixture of acrolein (23.17 g, 90% pure, 0.37 mol), $NaNO_2$ (33.1 g, 0.47 mol), and THF (150 mL). Stirring and cooling were maintained for 2.5 hr, and then water (50 mL) was added to dissolve solids. Layers were separated, and the aqueous layer was extracted with ether (three 70-mL portions). The combined organic layers were washed with saturated $NaHCO_3$ solution (two 70-mL portions), brine (two 50-mL portions), and water (20 mL). Drying over anhydrous $MgSO_4$ and concentration gave 19 g of 3-nitropropanal as an oil. A solution of the crude aldehyde in ether (100 mL) was treated with borane · dimethyl sulfide (230 mL of a 2 M solution in ether) added in nine portions over 10 min. The resulting mixture was stirred at room temperature for 12 hr, cooled to 0-5 °C, and treated cautiously with methanol (120 mL). Stirring was continued for 1 hr. Then, the mixture was concentrated at reduced pressure to yield 12 g of 3-nitro-1-propanol as an oil suitable for use in the next step.

3-Nitro-1-propanol (5.06 g, 48.1 mmol) was added over 2 min to a pre-prepared (under nitrogen, 1 hr) solution of triphenylphosphine (18.8 g, 72 mmol) and diisopropyl azodicarboxylate (DIAD; 14.5 g, 72 mmol) in benzene (300 mL), and the solution was stirred for 1 hr. Volatiles were stripped at reduced pressure into a dry ice-cooled receiver to remove the desired product from phosphorus-containing materials at low temperature (failure to do so resulted in none of the desired product). The last traces of product were entrained by adding three 25-mL portions of benzene to the distillation pot, followed each time by stripping. Kugelrohr redistillation of the combined distillates at atmospheric pressure gave 0.88 g (20% yield) of nitrocyclopropane contaminated with a little benzene. This procedure was not optimized but should be amenable to scale up if desired.

2.6 Synthesis of Compound 6: *trans*-1,2-Dinitrocyclopropane (DNCP).

Wade and co-workers' procedure[9] for the synthesis of *trans*-1,2-dinitrocyclopropane (compound **6**) was substantially improved for scale-up purposes. The original and the improved procedures employ 1,3-dinitropropane in DMSO solution. The original procedure used dimethylsodium as the base, and reaction temperature and time were crucial. The original procedure is strongly exothermic and would not be readily amenable to scale up.

The improved procedure involves treatment with 10 molar equivalents of sodium acetate[*] as a mild base and 3 molar equivalents of iodine. Ring closure takes place in approximately 2 hr. In our best run on a 100 mg scale, a 43% crude yield of compound **6,** which could be readily recrystallized to yield pure compound **6** (not optimized, small scale), was obtained.

When scaled up, the improved procedure gave pure product by recrystallization but provided a lower yield. A solution of 1,3-dinitropropane (2.0 g, 14.9 mmol) in DMSO (50 mL) was added dropwise over 5 min to a cooled solution containing sodium acetate (12.3 g, 149 mmol) and iodine (11.4 g, 45 mmol) in DMSO (200 mL). Cooling during the addition was performed so that the temperature did not rise above 30 ^{o}C. In one run where the reaction temperature was not controlled and rose to near 50 ^{o}C, a side product tentatively identified as 5-nitroisoxazole was formed in significant quantity. The resulting solution was poured into ice-cold brine (2 L). Extraction with ethoxylacetate (three 100-mL portions) followed by washing with brine (three 100-mL portions), drying over anhydrous Na_2SO_4, and concentration gave 1.86 g of crude product. The product was recrystallized from CCl_4-hexanes to give 223 mg of pure compound **6** and a second crop of 83 mg of fairly pure compound **6.** Chromatography of the mother liquor provided more product, which was combined with the second crop and recrystallized to yield 200 mg of pure compound **6** (423 mg total, 21% yield). The procedure was repeated two times to prepare a total of 1.2 g of compound **6**.

3. DETONATION EXPERIMENTS

Detonation studies were conducted on compounds **1-6** to determine which compounds would be best to use in follow-through devices. Most of the detonation studies involved using 25 mL of a nitromethane solution of the compound being tested and employing morpholine as a sensitizer. The solution was placed in a sample tube mounted on a plastic block (blast observation device). Polypropylene and high-density polyethylene blocks were used.

The sample tube was fitted at the top with a blast cap and explosive booster pellet placed touching the solution, and the device was detonated remotely (Figure 1). The observation block typically developed a crater from the ensuing blast. The size of the crater was measured by filling it with water and determining the volume of water. The results obtained are presented in Tables 2-6. A number of experiments involving detonation of sensitized nitromethane, not admixed with test compounds, were performed to develop reference standards. The results of the reference detonations are listed in Table 7.

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[*] It has been previously noted that potassium acetate functions in DMSO solution as a base capable of deprotonating nitro compounds.

Of the two kinds of blocks used for blast observation, the polypropylene blocks were deformed less under the test conditions. They routinely gave smaller reference craters and showed no crevices. For polypropylene blocks with a reference mixture, the craters ranged from 16.0-24.5 mL, with the mean crater size being 20.5 mL. Similar reference standards run with polyethylene blocks gave craters holding from 20.3-29.6 mL of water, with the mean crater size being 25.0 mL. In addition, the crater lips were somewhat more jagged for the polyethylene blocks, and in some sample runs, crevices were observed in the blocks.

Although, sensitized 4,5-dihydro-3-nitroisoxazole (compound **1**) was less powerful than sensitized nitromethane, the former did detonate. The resulting crater was only 42% as large as the mean reference crater. When compound **1** was admixed with nitromethane and morpholine sensitizer, a *more* powerful explosion than for either sensitized component by itself was noted (crater was 113% greater than the mean reference crater: four out of five reference craters were smaller, so there is an 80% confidence level for this result). For a more refined analysis, refer to Section 3.1. It appears that compound **1** in nitromethane produced a synergistic detonation.

Sensitized nitromethane solutions of 1,1-dinitroethane (compound **3**) gave very large craters. These were 154-160% greater than the mean reference crater. No reference crater was as large as that produced by detonation of compound **3**. This compound has a high nitro to carbon ratio (two nitro groups to two carbon atoms) and theoretically would be a good candidate for a powerful explosive.

Sensitized nitromethane solutions of 2,2-dinitropropane (compound **2**) (craters only 98% of the mean reference crater) and nitrocyclopropane (compound **5**) (crater only 104% of the mean reference crater) showed low potential based on these detonation studies. However, a sensitized nitromethane solution of 1,3-dinitropropane (compound **4**), which is isomeric with compound **2**, showed high potential (crater was 134% greater than the mean reference crater; no other reference crater was as large). This is surprising because isomers such as compounds **2** and **4** would be expected to produce similar results.

An attempt to detonate a sensitized solution containing nitroethane and 1,3-dinitropropane (compound **4**) was unsuccessful. Therefore, mixtures employing nitroethane rather than nitromethane are not good candidates for further investigation.

A sensitized nitromethane solution of *trans*-1,2-dinitrocyclopropane (compound **6**) gave the most promising results, since it formed a very large crater considering the size of the sample. Indeed, a 4-mL sample of compound **6** gave a crater 107% greater than the mean crater for 25 mL reference samples. Although the device used for compound **6** was not equivalent to the device used with the larger reference samples, this result is unequivocal. Compound **6** is a powerful explosive when admixed with nitromethane.

3.1 Detonation Statistics.

The performance of a sensitized nitromethane mixture of a given compound was determined by answering the following question. Did the mixture crater volume statistically exceed the reference crater volume? The test statistic "u," a function of the z-statistic (one-sided normal test) was determined in each case.[10] A formula for "u" follows:

$$u = z_{1-\alpha} \, (\sigma / \sqrt{n})$$

where "α " is the significance level (the probability of mistakenly finding a difference where none exists) and should always be as small as possible, and "z" is the cumulative normal distribution for a value of the standard normal variable $p = 1 - \alpha$. Values of "z" do not depend on the number of tests. Because only increased crater size was of interest, decisions were made based on a one-sided test. The variable "σ " denotes the population standard deviation, and "n" is the number of tests (typically 1). For a small number of tests, $3 < n < 10$, an estimate of "σ," denoted "s" is defined as $s = \text{range}/\sqrt{n}$. This formula can be used directly for the reference detonations where the range is the difference between the largest and the smallest crater. For comparison to the mixtures under study, it is assumed that a similar spread of crater volumes would result (*i.e.*, the reference and compounds under study have a similar standard deviation). This seems logical. The performance may vary, but the standard deviation should be similar for all the liquid explosives. If there is a difference, the more powerful explosive mixtures might give a slightly greater standard deviation. Thus, the statistical analysis is based on assumptions, which could be challenged but are at least reasonable.

3.2 Statistical Results.

Statistical results are provided in Tables 2 through 8 and Sections 3.2.1 through 3.2.6.

3.2.1 One-Sided Normal Test of Table 1, Entry 2: Compound **1**, **DHI**.

- Significance level: $\alpha = 0.25$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.75} = 0.67$
- Crater volume: $x = 23.1$
- Assumption of variability of the population: $\sigma = 3.80$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha}(\sigma/\sqrt{n}) = 0.67\,(3.80/\sqrt{1}) = 2.55$
- Test decision: $(x - m_o) > u$?

$$(23.1 - 20.5) = 2.6 > 2.55$$

- Decision: Crater exceeds that caused by detonation of the reference mixture. However, the probability of being mistaken, $\alpha = 0.25$, is somewhat high.

3.2.2 One-Sided Normal Test of Table 2, Entry 1: Compound **2**, **DNP**[1].

- Significance level: $\alpha = 0.25$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.75} = 0.67$
- Crater volume: $x = 24.6$
- Assumption of variability of the population: $\sigma = 4.65$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha} (\sigma/\sqrt{n}) = 0.67 (4.65/\sqrt{1}) = 3.11$
- Test decision: $(x - m_o) > u$?

  $(24.6 - 25.0) = -0.4 < 3.11$
- Decision: Crater does not exceed that caused by detonation of the reference mixture.

3.2.3 One-Sided Normal Test of Table 3, Entry 1: Compound **3**, **DNE**.

- Significance level: $\alpha = 0.05$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.95} = 1.645$
- Crater volume: $x = 31.5$
- Assumption of variability of the population: $\sigma = 3.80$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha} (\sigma/\sqrt{n}) = 1.645 (3.80/\sqrt{1}) = 6.25$
- Test decision: $(x - m_o) > u$?

  $(31.5 - 20.5) = 11.0 > 6.25$
- Decision: Crater significantly exceeds that caused by detonation of the reference mixture.

3.2.4 One-Sided Normal Test of Table 3, Entry 2: Compound **3**, **DNE**.

- Significance level: $\alpha = 0.05$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.95} = 1.645$
- Crater volume: $x = 32.8$
- Assumption of variability of the population: $\sigma = 3.80$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha} (\sigma/\sqrt{n}) = 1.645 (3.80/\sqrt{1}) = 6.25$
- Test decision: $(x - m_o) > u$?

  $(32.8 - 20.5) = 12.3 > 6.25$
- Decision: Crater significantly exceeds that caused by detonation of the reference mixture.

3.2.5 One-Sided Normal Test of Table 4, Entry 1: Compound **4**, **DNP**[2].

- Significance level: $\alpha = 0.05$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.95} = 1.645$
- Crater volume: $x = 33.4$
- Assumption of variability of the population: $\sigma = 4.65$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha} (\sigma / \sqrt{n}) = 1.645 (4.65/\sqrt{1}) = 7.65$
- Test decision: $(x - m_o) > u$?

  $(33.4 - 25.0) = 8.4 > 7.65$
- Decision: Crater exceeds that caused by detonation of the reference mixture. The confidence level, $\alpha = 0.05$, is quite high.

3.2.6 One-Sided Normal Test of Table 5, Entry 1: Compound **5**, **NCP**.

- Significance level: $\alpha = 0.05$
- Cumulative normal distribution: $z_{1-\alpha} = z_{0.95} = 1.645$
- Crater volume: $x = 25.9$
- Assumption of variability of the population: $\sigma = 4.65$
- Size of population: $n = 1$
- Test statistic: $u = z_{1-\alpha} (\sigma / \sqrt{n}) = 1.645 (4.65/\sqrt{1}) = 7.65$
- Test decision: $(x - m_o) > u$?

  $(25.9 - 25.0) = 0.9 < 7.65$
- Decision: Crater does not exceed that caused by detonation of the reference mixture.

4. CALORIMETRY

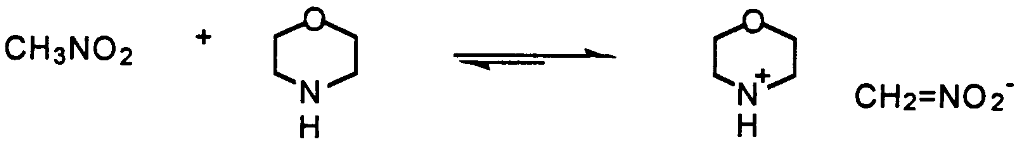
Nitromethane and compounds **1**, **2**, **4**, and **5** were combusted in a bomb calorimeter to determine heat of combustion. The calorimeter was charged with a 300-mg sample in all but one case, after which oxygen was introduced to 30 psi. The sample was combusted, and the temperature rise of the surrounding water bath was measured with an accurate computer-monitored thermocouple. The resulting calorimetry plots are presented in Figures 2-6. Results are summarized in Table 9 where the best candidates for high-energy performance are shown to be compounds **4** and **5.** These two compounds gave the highest heat of combustion per gram. Compound **1** gave a lower heat of combustion than nitromethane (agreed with the detonation results). Compound **2** also gave a lower heat of combustion than nitromethane; but, this result is somewhat questionable since only 128.9 mg of sample was available for combustion. The remainder was consumed in earlier detonation studies.

5. CONCLUSIONS

Based on the detonation studies, the best candidate explosive mixtures are those employing 1,1-dinitroethane (compound **3**) and *trans*-1,2-dinitrocyclopropane (compound **6**). These materials gave the largest craters in the detonation studies. Although compound **6** was not directly compared to a reference, detonation of its 4-mL sample resulted in a larger crater than the mean of the 25 mL reference samples. Presumably, a more powerful detonation wave was generated, although owing to the smaller sample size, the detonation wave was likely of shorter duration. It would seem that blast pressure is more important in deforming the observation blocks than the blast duration.

Compound **4** also showed considerable promise in the detonation studies. Surprisingly, compound **2** did not meet expectations. The calorimetry studies showed a higher heat of combustion for compound **4** than for compound **2**, although only a small sample of it was available for study. Thus, compound **4** with the nitro groups on separate carbon atoms proved the more energetic material. Additional candidates should be chosen based on this consideration.

Those compounds, which had acidic hydrogens and formed nitronate salts with the sensitizer, appeared to be the best candidates based on measurements in the detonation studies. Nitromethane with its acidic hydrogens would be expected to form a salt with the sensitizer (Equation 1), and it is theorized that salt formation may be responsible for the sensitizer's effect. Compounds **3**, **4**, and **6** could form similar salts,[11] and all were observed to be powerful explosives when admixed with nitromethane. Conversely, compound **2**, which had no acidic hydrogens and did not form salt, did not increase the explosive power of nitromethane when admixed with it.



(1)

Compound **1,** when admixed with nitromethane, gave a *more* powerful explosion than was observed for either component by itself. The confidence level for this result is 80%. It seems likely that these materials develop a synergistic explosive effect. More study of this mixture and additional explosive mixtures would seem warranted based on this observation.

Compound **5** showed low potential based on the detonation study but high promise in the calorimetry study. Theoretically, it would be a good candidate because of the ring strain inherent in a 3-membered ring (about 30 kcal/mol). However, nitrocyclopropane (compound **5**) has only one nitro group for three carbons. When combusted, it provides considerable energy; but, when detonated, it would not necessarily be powerful because of the low nitro-to-carbon ratio. It is noteworthy that compound **6**, which has two nitro groups for three carbons and also has ring strain, was confirmed as a powerful explosive addant to nitromethane in the detonation study.

Compound **5** is not sufficiently acidic to form a salt with a morpholine sensitizer (compound **5** has an abnormally low acidity).[12] This may also explain the discrepancy between the calorimetry and detonation studies for the compound.

6. RECOMMENDATIONS FOR FURTHER STUDY

More study is recommended of synergistic effects with components of explosive mixtures based on the observation of a likely synergistic effect between nitromethane and 4,5-dihydro-3-nitroisoxazole (compound **1**). A theoretically interesting mixture would be nitrocyclopropane (compound **5**), which needs more nitro groups, and 1,1-dinitroethane (compound **3**), which has two nitro groups for two carbons. Alternatively, tetranitromethane and nitrocyclopropane might provide a powerful explosive mixture.

More study of *trans*-1,2-dinitrocyclopropane (compound **6**) explosive mixtures is recommended based on its detonation result. This compound should be prepared in larger quantity, and detonation studies should be performed on mixtures with nitromethane and 1,1-dinitroethane.

Additional candidate explosives might be examined including 1,2-dinitroethane and 1,2,3-trinitropropane. T*rans*-1,2-dinitrospiropentane with 70 kcal/mol of ring strain might also prove of interest but is difficult to synthesize.[11]

Application of a sensitized mixture of either nitromethane and compound **3** or nitromethane and compound **6** to actual weapons production should be considered. Decisions on storage time and temperature requirements, sensitivity requirements, and production cost requirements would be necessary, and additional studies to determine if these mixtures meet the requirements would need to be performed.

It should be noted that 1,1-dinitroethane in nitromethane, which showed high detonation capability, could be produced on a large scale relatively cheaply. This mixture should *definitely* be considered for military application.

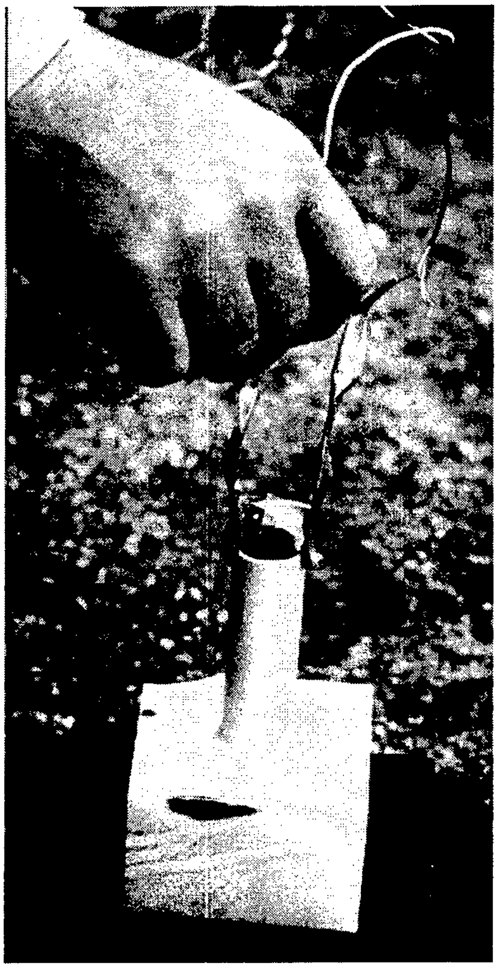


Figure 1. Detonation Apparatus

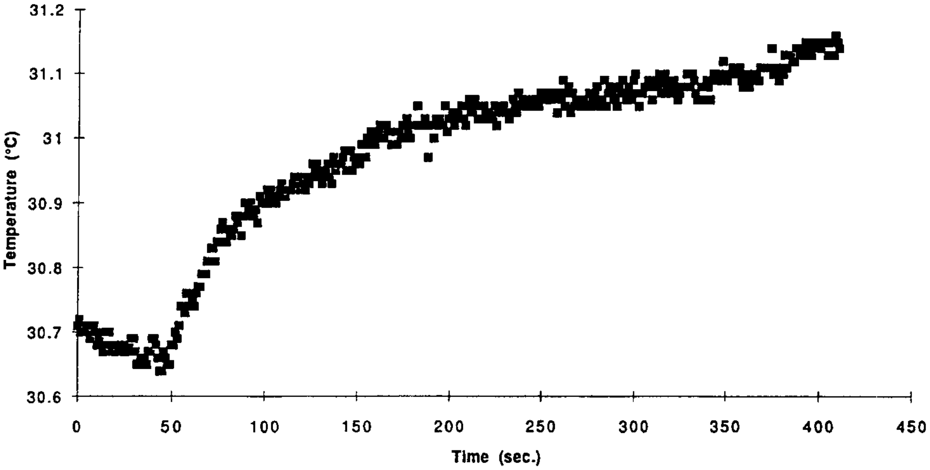


Figure 2. Calorimetry Study of Nitromethane

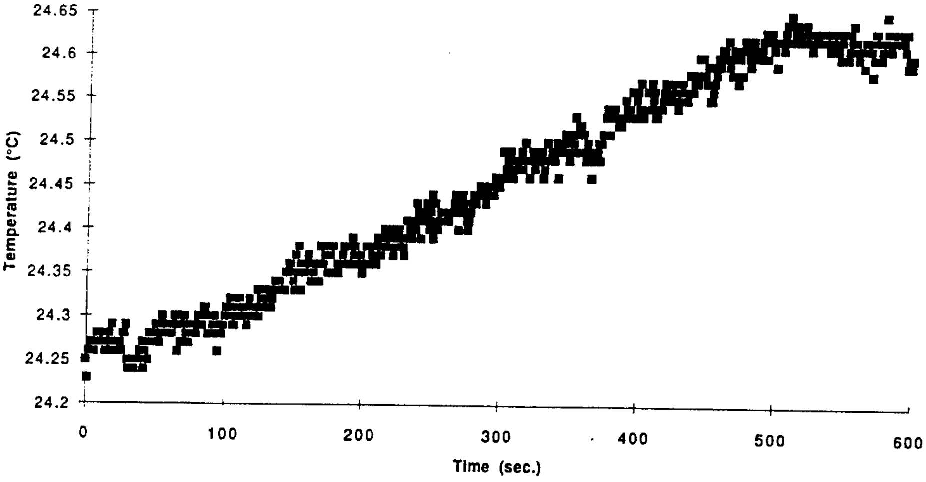


Figure 3. Calorimetry Study of 4,5-Dihydro-3-nitroisoxazole (1)

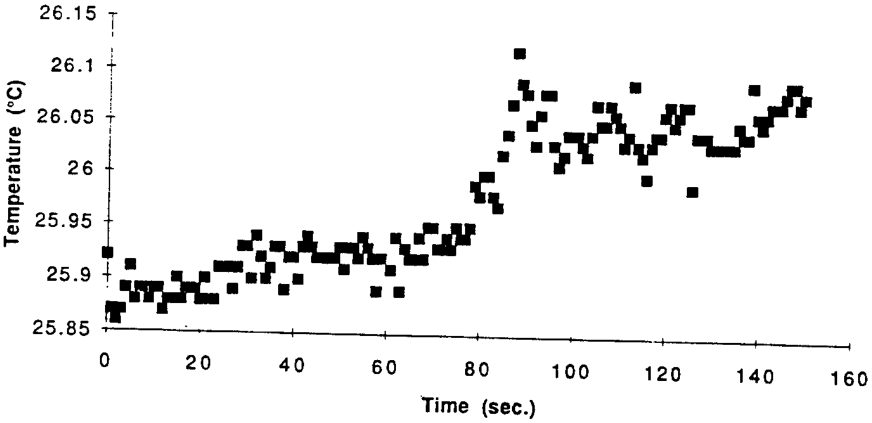


Figure 4. Calorimetry Study of 2,2-Dinitropropane[1] (2)

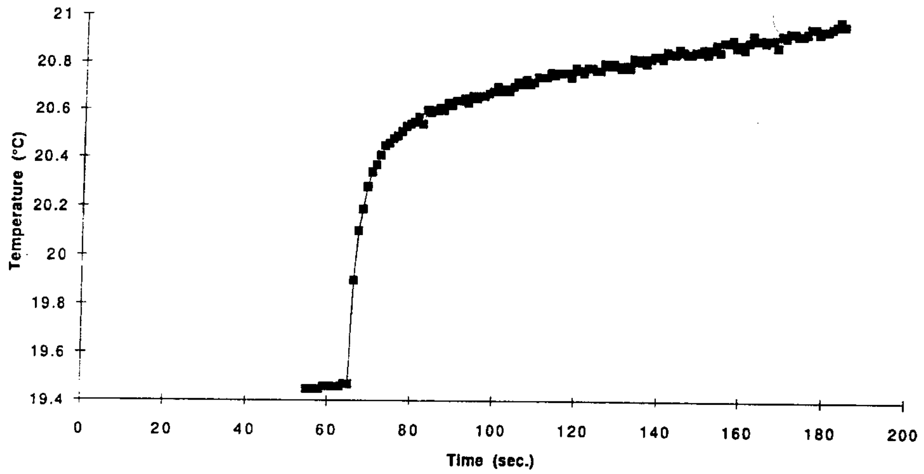


Figure 5. Calorimetry Study of 1,3-Dinitropropane[2] (4)

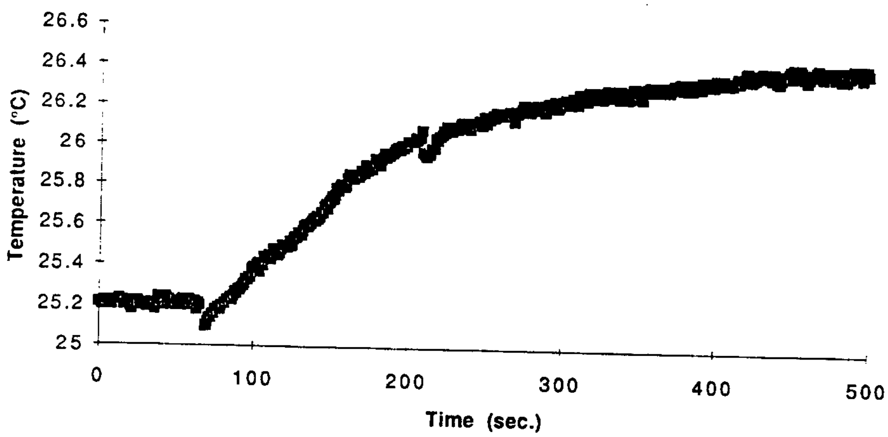
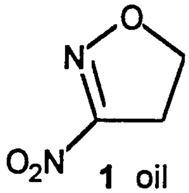


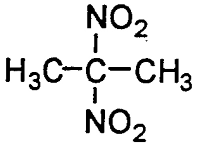
Figure 6. Calorimetry Study of Nitrocyclopropane (5)

Table 1. Shaped-Charge, Follow-Through Candidate Explosive Compounds



1 oil

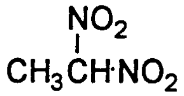
4,5-dihydro-3-nitroisoxazole
bp 114-118 °C (4 mmHg)



$H_3C-C(NO_2)_2-CH_3$

2 solid

2,2-dinitropropane
mp 53 °C



$CH_3CH(NO_2)NO_2$

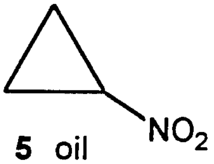
3 oil

1,1-dinitroethane
bp 185-186 °C
bp 64-66 °C (4 mmHg)

$O_2N-CH_2CH_2CH_2-NO_2$

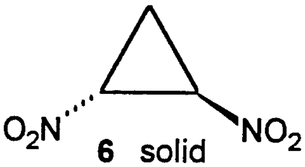
4 oil

1,3-dinitropropane
bp 109-112 °C (19 mmHg)



5 oil

nitrocyclopropane
bp 143-145 °C
bp 65-67 °C (58 mmHg)



6 solid

trans-1,2-dinitrocyclopropane
mp 61 °C

Table 2. Detonation Results for 4,5-Dihydro-3-nitroisoxazole (**1**)

Entry	Mixture[a] (parts by volume)	Crater Volume[b] (mL)	% relative blast size sample/reference
1	0NM/0MOR/25DHI	8.64	42
2	18NM/1MOR/6DHI	23.1	113
reference mixture	23.75NM/1.25MOR Reference mixture	20, 16.0, 20.9, 24.5, 21.3	100

[a] NM = nitromethane, MOR = morpholine, DHI = 4,5-dihydro-3-nitroisoxazole
[b] Polypropylene block

Table 3. Detonation Results for 2,2-Dinitropropane (**2**)

Entry	Mixture[a] (parts by volume)	Crater Volume[b] (mL)	% relative blast size sample/reference
1	18NM/1MOR/6DNP'	24.6	98
2	16NM/1MOR/8DNP'	24.4[c]	98
reference mixture	24NM/1MOR Reference mixture	26.9, 23.0, 29.6, 20.3	100

[a] NM = nitromethane, MOR = morpholine, DNP' = 2,2-dinitropropane
[b] High density polyethylene block
[c] Crater lip heavily damaged in this run: volume perhaps low due to leakage.

Table 4. Detonation Results for 1,1-Dinitroethane (**3**)

Entry	Mixture[a] (parts by volume)	Crater Volume[b] (mL)	% relative blast size sample/reference
1	16NM/1MOR/8DNE	31.5	154
2	18NM/1MOR/6DNE	32.8	160
reference mixture	23.75NM/1.25MOR Reference mixture	20, 16.0, 20.9, 24.5, 21.3	100

[a] NM = nitromethane, MOR = morpholine, DNE = 1,1-dinitroethane
[b] Polypropylene block

Table 5. Detonation Results for 1,3-Dinitropropane (**4**)

Entry	Mixture[a] (parts by volume)	Crater Volume[b] (mL)	% relative blast size sample/reference
1	18NM/1MOR/6DNP	33.4	134
2	18NE/1MOR/6DNP	No detonation	0
reference mixture	24NM/1MOR Reference mixture	26.9, 23.0, 29.6, 20.3	100

[a] NM = nitromethane, MOR = morpholine, DNP = 1,3-dinitropropane, NE = nitroethane
[b] High density polyethylene block

Table 6. Results for Nitrocyclopropane (**5**)

Entry	Mixture[a] (parts by volume)	Crater Volume[b] (mL)	% relative blast size sample/reference
1	18NM/1MOR/6NCP	25.9	104
reference mixture	24NM/1MOR Reference mixture	26.9, 23.0, 29.6, 20.3	100

[a] NM = nitromethane, MOR = morpholine, NCP = nitrocyclopropane
[b] High density polyethylene block

Table 7. Results for *trans*-1,2-Dinitrocyclopropane (**6**)

Entry	Mixture[a]	Crater Volume[b] (mL)	Comments
1	NM/MOR/DNCP[c]	26.7	for just 4 mL!
blank	Water, 4.0 mL Reference blank	Small dent, no crater in block.	blast cap did not cause result

[a] NM = nitromethane, MOR = morpholine, DNCP = *trans*-1,2-dinitro-cyclopropane
[b] High density polyethylene block
[c] 3.13 mL of 24NM/1MOR reference mixture dissolving 1.0005 g of DNCP: total volume 4 mL

Table 8. Statistical Treatment of Reference Detonations

Block Material	Range (mL)	n	$\sigma \cong s = \text{range}/\sqrt{n}$	Mean Crater Volume, m_o, mL
polypropylene	8.5	5	3.80	20.5
polyethylene	9.3	4	4.65	25.0

Table 9. Calorimetry Results

Material	Sample Wt, mg	Observed ΔT, °C	ΔT per gram, °C/g	% ΔT of Reference
NM[a]	298.7	0.50	1.67	100
1	306.8	0.36	1.17	70
2	128.9[b]	0.17	1.32	79
4	313.6	1.40	4.46	267
5	310.5	1.20	3.86	231

[a] NM = nitromethane

[b] very small sample size: accuracy questionable

Blank

LITERATURE CITED

1. Wade, P.A., J. Org. Chem. Volume 43, p 2020 (1978).

2. Noyes, W.A., "Prepared Analogously to *n*-Butyl Nitrite," In Organic Synthesis, Volume 2, p 108, John Wiley & Sons, New York, NY, 1943.

3. Kornblum, N., Singh, H.K., and Kelly, W.J., J. Org. Chem. Volume 48, p 332 (1983).

4. Kaplan, R.B., and Shechter, H., J. Am. Chem. Soc. Volume 83, p 3535 (1961).

5. Feuer, H., and Leston, G., Organic Synthesis Volume 5, p 368, N. Rabjohn, Ed., John Wiley & Sons, New York, NY, 1963.

6. Kai, Y., Knochel, P., Kwiatkowski, S., Dunitz, J.D., Oth, J.F.M., and Seebach,D., Helv. Chim. Acta Volume 65, p 137 (1982).

7. Yu, J., Falck, J.R., and Mioskowski, C., J. Org Chem. Volume 57, p 3757 (1992).

8. Öhrlein, R., Schwab, W., Ehrler, R., and Jager, V., Synthesis, p 535 (1986).

9. Wade, P.A., Dailey, W.P., and Carroll, P.J., J. Am. Chem. Soc. Volume 109, p 5452 (1987).

10. Wade, P.A., Ph. D. dissertation, Purdue University, West Lafayette, IN, 1973.

11. Engineering Design Handbook, Experimental Statistics Section 1, Basic Concepts and Analysis of Measurement Data, AMCP 706-110, U. S. Army Material Command, December 1969.

12. Wade, P.A., Kondracki, P.A., and Carroll, P.J., J. Am. Chem. Soc. Volume 113, p 8807 (1991).

13. Bordwell, F.G., Bartmess, J.E., and Hautala, J.E., J. Org. Chem. Volume 43, p 3113 (1978).