1-(2',4',6'-Trinitrophenyl)imidazoles and -1,2,4-triazoles as Energetic Materials

by

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MARCH 1994

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Naval Air Warfare Center Weapons Division

FOREWORD

The Navy has a continuing need for new insensitive but powerful energetic materials. The synthesis and properties of 1-(2',4',6'-trinitrophenyl)imidazoles and -1,2,4-triazoles were investigated in an effort to satisfy that need and to provide further insight into structure/sensitivity correlations in polynitroazaheterocycles.

This report has been reviewed for technical accuracy by Richard A. Hollins.

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(U) A series of 1-(2',4',6'-trinitrophenyl)imidazoles and -1,2,4-triazoles has been prepared. These compounds have been chemically characterized by infrared spectroscopy, mass spectrometry, and $^1$H- and $^{13}$C-nuclear magnetic resonance (NMR) spectroscopy, and their physical and explosive properties have been examined. The measured densities correspond with those predicted, and increase with increasing the degree of nitration. The impact sensitivities are less than those of 1-(2',4',6'-trinitrophenyl)benzotriazoles, but increase with the degree of nitration (or increasing oxygen balance). Higher levels of nitration also induce reduced hydrolytic stability, and the desired 1-(2',4',6'-trinitrophenyl)-2,4,5-trinitroimidazole and -3,5-dinitro-1,2,4-triazole could not be prepared. Extrapolation of the results obtained suggests that they would be quite sensitive explosives.

Explosives, Synthesis, Imidazoles, Triazoles, Density, Sensitivity, Stability
CONTENTS

Introduction ............................................................................................................ 3

Results and Discussion ........................................................................................ 5
  Synthesis of 1-Picrylimidazoles ........................................................................ 5
  Synthesis of 1-Picyl-1,2,4-triazoles ................................................................ 8
  Physical and Explosive Properties of 1-Picrylimidazoles and 1,2,4-Trazoles ... 10
  Alternative Synthetic Approaches to 1-Picyl-2,4,5-trinitroimidazole and -3,5-dinitro-1,2,4-triazole .................................................................................. 12

Conclusions ............................................................................................................ 16

Experimental ........................................................................................................... 17
  1-(2',4',6'-Trinitrophenyl)imidazole (9) ............................................................ 17
  4-Nitro-1-(2',4',6'-trinitrophenyl)imidazole (11) ................................................. 17
  4,5-Dinitro-1-(2',4',6'-trinitrophenyl)imidazole (13) .......................................... 18
  2-Nitro-1-(2',4',6'-trinitrophenyl)imidazole (15) ................................................. 18
  2,4-Dinitro-1-(2',4',6'-trinitrophenyl)imidazole (16) ........................................... 18
  Pathway A ......................................................................................................... 18
  Pathway B ......................................................................................................... 19
  1-(2',4',6'-Trinitrophenyl)-1,2,4-triazole (22) ..................................................... 19
  3-Nitro-1-(2',4',6'-trinitrophenyl)-1,2,4-triazole (25) .......................................... 19
  3,5-Dinitro-1-phenyl-1,2,4-triazole (33) ............................................................. 20
  3,5-Diamino-1-(2'-nitrophenyl)-1,2,4-triazole (34) ............................................. 20
  3,5-Diamino-1-(4'-nitrophenyl)-1,2,4-triazole (35) ............................................. 21
  Oxidation of 3,5-Diamino-1-(4'-Nitrophenyl)-1,2,4-triazole (35) ................. 21

References .............................................................................................................. 23

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INTRODUCTION

Over the past decade or so, research has been carried out in our laboratories, with some success, into the synthesis of new energetic materials to be utilized as explosive and propellant ingredients. The aims of this work have been to couple high density (approaching 2.0 grams/cubic centimeter \((g/cm^3)\)) with high energy (velocity of detonation exceeding 9000 meters/second \((m/s)\), detonation pressure approaching 400 kilobars \((kbar)\), and a specific impulse of 270 s) and/or enhanced stability and insensitivity to such stimuli as impact, friction, and electrostatic discharge. This research has fallen largely in the areas of polynitrobenzenes (and related compounds) and polycyclic and caged nitramines. Prince among the polynitrobenzenes was hexanitrobenzene (Reference 1), with a density of 1.99 \(g/cm^3\) and a velocity of detonation of 9100 m/s, but it was quite sensitive, with a drop height of 11 cm, and it proved to be hydrolytically unstable. Stability and insensitivity could be improved with the related benzofuroxans (Reference 2), but at the cost of somewhat degraded performance. More recently the caged nitramine CL-20 has proven to have exceptional performance properties, and it appears to be quite stable, but it is also rather sensitive to environmental stimuli such as impact, friction, and electrostatic discharge.

It was hoped that perhaps useful materials might be obtained from the class of polynitroheterocycles, and particularly azaheterocycles, which might simplistically be regarded as being intermediate between the aromatics and the nitramines. It was envisaged that such compounds would also be dense and energetic, but that the properties of the heterocyclic skeleton might confer added stability and insensitivity. Unfortunately, the methods applied so successfully to the synthesis of polynitrobenzenes have proven inappropriate for the polynitroheterocycles. Further, there is not the comprehensive body of knowledge on which to base structure/property relations and from which to predict trends in stability and insensitivity.

We recently reported the unexpected formation of 1-phenyl-5,7-dinitrobenezotriazole in high yield on attempted nitration of 2-amino-4,6-dinitrodiphenylamine. We took advantage of this serendipitous result to investigate the explosive properties of various substituted benzotriazoles, and concluded that 1-(2',4',6'-trinitrophenyl)benzotriazoles (1-picrylbenzotriazoles) (1) owed their sensitivity to the picryl-N-N=N moiety—i.e., that this structural feature contains the "trigger linkage" at which the initiation reaction occurs (Reference 3). This conclusion was supported by subsequent examination of 1-picrylbenzimidazoles (2). These compounds are closely related to the 1-picrylbenzotriazoles, but contain the Pic-N-CH=N functional grouping in place.
of the Pic-N-N=N, and they are considerably less sensitive. For example, they have impact sensitivities of ca. 90 cm, compared with 15-40 cm for 1-picryl-benzotriazoles. It was proposed that the initiation reaction in the 1-picryl-benzotriazoles occurred by elimination of molecular nitrogen, leaving behind a radical species to propagate further reaction (Reference 4).

If this result may be extrapolated to other related heterocyclic ring systems, it may provide a strategem for designing powerful but insensitive explosives, simply by avoiding the Pic-N-N=N functionality. There appears to be support for this hypothesis in results from other laboratories. Thus, Australian research showed that picryl-5-nitrotetrazole (3) (the position of the picryl group could not be assigned unequivocally) is a sensitive primary or initiating explosive (Reference 5). Further, Neuman prepared several pairs of 1- and 2-picryl-1,2,3-triazoles and found in each case that the 1-picryl isomer (4) was sensitive to impact while the 2-picryl isomer (5) was insensitive (Reference 6). This latter result was rationalized by invoking a mechanism similar to that described above for the initiation of the 1-picryl-1,2,3-triazoles (4) (Reference 7).

In order to further test this hypothesis, and in an attempt to develop a new class of energetic materials, 1-picryl-2,4,5-trinitroimidazole (6) and 1-picryl-3,5-dinitro-1,2,4-triazole (7) were proposed as target molecules for synthetic efforts. These molecules have empirically predicted densities of 1.89 and 1.86 g/cm$^3$ (Reference 8), velocities of detonation of 8420 and 8480 m/s, and detonation pressures of 329 and 336 kbar, respectively (Reference 9). They also lack the (apparently) sensitizing Pic-N-N=N functional grouping, and therefore, should be relatively insensitive to environmental stimuli such as impact, friction, and electrostatic discharge.
RESULTS AND DISCUSSION

SYNTHESIS OF 1-PICRYLIMIDAZOLES

Chemical structures were assigned on the basis of a combination of spectroscopic techniques, including infrared spectra, $^1$H- and $^{13}$C-NMR spectra and mass spectra (electron impact and, where necessary, chemical ionization). The synthetic approach used initially was that previously employed by Coburn and Neuman for the preparation of several picrylimidazoles (Reference 10) and modified successfully for the synthesis of 1-picrylbenzimidazoles (Reference 4). Thus, imidazole (8) was dissolved in dimethylformamide and treated with picryl fluoride at ambient temperature. Quenching in water gave the desired 1-picrylimidazole (9) in good yield. It seems likely that the reaction proceeded essentially to completion, the limiting factor being some slight solubility of the product in water. There is some evidence, however, that 9 may show some hydrolytic instability.

Nitration of imidazole (8) using a mixture of 96% sulfuric acid and 70% nitric acid under reflux afforded 4-nitroimidazole (10), as described by Novikov (Reference 11). Once again, dissolution of 10 in dimethylformamide and treatment with picryl fluoride at ambient temperature, followed by quenching in water, afforded 4-nitro-1-picrylimidazole (11) in excellent yield.
Nitration of imidazole (8) under more forcing conditions, using a mixture of 96% sulfuric acid and 90% nitric acid under reflux, gave 4,5-dinitroimidazole (12), again as described by Novikov (Reference 11). As previously, dissolution of 12 in dimethylformamide and then treatment with picryl fluoride at ambient temperature followed by quenching in water afforded 4,5-dinitro-1-picrylimidazole (13) in virtually quantitative yield.

2-Nitroimidazole (14) is available commercially, being known better as the antibiotic, azomycin. This material also reacts readily with picryl fluoride in dimethylformamide giving 2-nitro-1-picrylimidazole (15), this time in moderate yield (Reference 10). Once again, the limiting factor is probably the solubility of the product in water. Rapid nitration of (15) in a mixture of 96% sulfuric acid and 90% nitric acid under reflux gave a modest yield of 2,4-dinitro-1-picrylimidazole (16); prolonged reaction or attempted nitration under more forcing conditions simply led to decomposition. A more efficient synthesis of 16 is achieved by reaction of 2,4-dinitroimidazole (18) with picryl fluoride in dimethylformamide. (2,4-Dinitroimidazole (18) may be prepared by nitration of 8 or 10 with nitric acid in acetic anhydride to give 1,4-dinitroimidazole (17), followed by thermal rearrangement in toluene or chlorobenzene under reflux (Reference 12). This compound has been proposed as an inexpensive, insensitive explosive (Reference 13) and has been the subject of investigations at both Los Alamos National Laboratory (LANL), Los Alamos, New Mexico, and Lawrence Livermore National Laboratory (LLNL), Livermore, Calif. However, material prepared at China Lake, although insensitive to friction (18/20 no fires at 1000 pounds (lb)) and to electrostatic discharge (10/10 no fires at 0.25 joules (J)), had an impact sensitivity of only 34 cm.)
2,4,5-Trinitroimidazole (20) cannot be obtained by direct nitration of imidazole (8). However, it can be prepared by nitration of 2,4,5-triiodoimidazole (19) (Reference 14), prepared in turn by iodination of imidazole under alkaline conditions (Reference 15), but in any case simple coupling of 20 with picryl fluoride did not lead to the desired 2,4,5-trinitro-1-picrylimidazole (6).
SYNTHESIS OF 1-PICRYL-1,2,4-TRIAZOLES

In an exactly analogous manner, 1,2,4-triazole (21) reacted with picryl fluoride in dimethylformamide at ambient temperature to give 1-picryl-1,2,4-triazole (22) in moderate yield. Interestingly, while the imidazole protons in 9, 11, and 15 are coupled, those in the triazole (20) show no coupling, and H₃ and H₅ appear in the $^1$H-NMR as simple singlets in both acetone-d$_6$ and DMSO-d$_6$. 

$$
\text{PicF} + 21 \rightarrow 22
$$
3-Nitro-1,2,4-triazole (24) was conveniently prepared by diazotization of 3-amino-1,2,4-triazole (23) and treatment with excess nitrite ion (Reference 16). In the now familiar fashion, 24 reacted with picryl fluoride in dimethylformamide at ambient temperature to give the expected 3-nitro-1-picryl-1,2,4-triazole (25) in good yield. It was noted, however, that 25 is hydrolytically unstable, yielding 24 and picric acid on reflux in 95% ethanol, on recrystallization from ethanol/acetone, or even on standing in slightly moist acetone at ambient temperature.

\[
\begin{align*}
\text{NH}_2 \quad \text{NO}_2 \\
\text{NaNO}_2 \quad \text{AcOH/H}_2\text{SO}_4 \\
\text{23} & \xrightarrow{\text{24}} \\
\text{H} & \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\end{align*}
\]

Diazotization of 3,5-diamino-1,2,4-triazole (26) in the presence of excess nitrite ion also leads to 3,5-dinitro-1,2,4-triazole (27) (References 16 and 17). However, as was the case with the fully nitrated imidazole (20), dissolution in dimethylformamide and treatment with picryl fluoride did not lead to the desired 1-picryl derivative (7).

\[
\begin{align*}
\text{NH}_2 \quad \text{H}_2\text{N} \\
\text{H} & \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\end{align*}
\]
The physical and explosive properties, both predicted and measured, of the picrylimidazoles and picryltriazoles prepared in this program are presented in Table 1. Densities were predicted using the empirical "group additivity" method of Holden, assuming that the heterocycle is nonaromatic (Reference 8); they were measured experimentally by the gas comparison pycnometry method using a Systems Science and Software Type 6102-28 instrument.

Oxygen balance (OB<sub>100</sub>) was calculated using the Kamlet and Adolph expression (Reference 18)

\[
OB_{100} = 100 \left( \frac{2n_O - n_H - 2n_C - 2n_{COO}}{MW} \right)
\]

where
- \( n_O \) = number of oxygen atoms,
- \( n_H \) = number of hydrogen atoms,
- \( n_C \) = number of carbon atoms,
- \( n_{COO} \) = number of carboxyl groups, and
- \( MW \) = molecular weight.

Velocity of detonation and detonation pressure were calculated using the simple empirical method of Rothstein and Petersen (Reference 9), which requires no prior knowledge of any physical or thermodynamic properties.

Impact sensitivities were measured at the Naval Air Warfare Center Weapons Division (NAWCWPNS) either in the Research Department (C0235) or in the Ordnance Systems Department (C27) using a Bureau of Mines machine, the Type 12 tool, and a 2.5 kilogram (kg) drop weight. The explosive (35 milligrams (mg)) is placed in a roughly conical pile on a 1-inch square of garnet paper and placed on the polished, flat tool steel anvil. The flat, polished tool steel striker is placed on top of the sample and a 2.5 kg weight is dropped from a predetermined height onto the striker. The result of the event, explosion or otherwise, is determined by a combination of sound, smell, and visual inspection of the sample and paper. The drop height is varied according to the Bruceton "staircase" method, the height being decreased if the previous event
was an explosion or increased if it was not. Drop heights are equally spaced in the logarithm of the height at 0.1 log unit intervals. (The log of a 10-cm drop is taken as 1.0.) A sequence of 25 tests is carried out, and the result is expressed as \( h_{50\%} \), the height at which 50% of tests result in explosions. The impact sensitivity of cyclotrimethylenetrinitramine (RDX) is 25 cm on the Research Department machine and 21 cm on the Ordnance Systems Department machine.

TABLE 1. Physical and Explosive Properties of 1-Picrylimidazoles and 1-Picryl-1,2,4-triazoles.

<table>
<thead>
<tr>
<th>Compound number</th>
<th>Density, g/cm(^3)</th>
<th>Oxygen balance, OB(_{100})</th>
<th>Impact sensitivity, ( h_{50%} ), cm</th>
<th>Velocity of detonation, ( V ) of D, m/s</th>
<th>Detonation pressure, ( P_{D1} ), kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1.66</td>
<td>1.67</td>
<td>-3.94</td>
<td>&gt;150</td>
<td>6640</td>
</tr>
<tr>
<td>11</td>
<td>1.74</td>
<td>1.71</td>
<td>-1.85</td>
<td>53.7</td>
<td>7430</td>
</tr>
<tr>
<td>13</td>
<td>1.81</td>
<td>1.79</td>
<td>-0.27</td>
<td>50.2</td>
<td>7990</td>
</tr>
<tr>
<td>15</td>
<td>1.74</td>
<td>1.72</td>
<td>-1.85</td>
<td>50(^a)</td>
<td>7430</td>
</tr>
<tr>
<td>16</td>
<td>1.81</td>
<td>1.78</td>
<td>-0.27</td>
<td>34(^a)</td>
<td>7990</td>
</tr>
<tr>
<td>6</td>
<td>1.87</td>
<td></td>
<td>+0.48</td>
<td>8420</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1.69</td>
<td>1.68</td>
<td>-2.86</td>
<td>97.8</td>
<td>7320</td>
</tr>
<tr>
<td>25</td>
<td>1.77</td>
<td>1.73</td>
<td>-0.93</td>
<td>64.7</td>
<td>8000</td>
</tr>
<tr>
<td>7</td>
<td>1.84</td>
<td></td>
<td>+0.54</td>
<td>8480</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Measured on the Ordnance Systems Department machine.

The 1-picrylimidazoles and 1,2,4-triazoles prepared in this study show the expected increase in density with increase in the extent of nitration about the heterocyclic ring. Further, there is reasonable agreement of the experimental densities obtained by gas pycnometry with those predicted by Holden’s method (Reference 8), although the experimental densities are consistently a little lower. This is probably a reflection of the heterocyclic and picryl rings being orthogonal, possibly combined with some steric interaction between nitro groups on the two rings; a similar effect was observed in the series of 1-picrylbenzimidazoles and -benzotriazoles.

The 1-picrylimidazoles and -1,2,4-triazoles also show an increase in impact sensitivity (i.e., a decrease in the drop height, \( h_{50\%} \), required to initiate explosive reaction in the sample) with the degree of nitration about the heterocyclic ring, and hence with oxygen balance. This is quite different from the behavior of the 1-picrylbenzotriazoles (Reference 3), whose impact sensitivities were little affected by oxygen balance. Indeed, the same can be
said for other classes of sensitive compounds, such as the diazophenols (Reference 19), which also have a clearly defined "trigger linkage." (On the other hand, the impact sensitivity of the 1-picrylbenzimidazoles is significantly affected by oxygen balance and the degree of nitration (Reference 4).) One implication of this observation is that the chemical reaction involved in impact initiation of the 1-picrylimidazoles and -1,2,4-triazoles probably involves cission of a nitro group, perhaps from the heterocyclic ring. Another implication is that, by extrapolation of the observed trends, the fully nitrated target molecules 6 and 7 may well prove to be sensitive explosives, even if they could be prepared. (It should be recalled, however, that they also have a much larger oxygen balance than the 1-picrylbenzimidazoles and benzotriazoles.) They would almost certainly not be the insensitive powerful energetic materials desired, and it appears that powerful but insensitive explosives perhaps cannot be devised simply by eliminating known "trigger linkages," such as the Pic-N-N=N moiety, and loading up with other explosophores such as nitro groups.

ALTERNATIVE SYNTHETIC APPROACHES TO 1-PICRYL-2,4,5-TRINITROIMIDAZOLE AND -3,5-DINITRO-1,2,4-TRIAZOLE

Failure to obtain the 1-picryl-substituted, pernitrated heterocycles 6 and 7 by simple coupling of the parent nitroheterocycle with picryl fluoride was a significant disappointment, since these compounds were the primary synthetic targets. The principal product in each case was picric acid, but it was unclear whether this arose from hydrolysis of the target compounds during aqueous work-up or directly from hydrolysis of the picryl fluoride starting material. It is to be recalled that 3-nitro-1-picryl-1,2,4-triazole (25) is sensitive to hydrolysis during attempts at recrystallization, and some of the imidazole derivatives also showed some signs of hydrolytic instability. 2,4,5-Trinitroimidazole (20) and 3,5-dinitro-1,2,3-triazole (27) are both hygroscopic; therefore, every effort was made to dry these reagents and the solvent, and to exclude moisture from the reaction mixture; aqueous work-up still yielded only picric acid.

The alkali metal salts (sodium and potassium) do not exhibit this hygroscopicity, and are, therefore, somewhat easier to handle. However, use of these salts in reaction with picryl fluoride in dimethylformamide did not change the course of the reaction, and only picric acid was recovered after work-up. An attempt was made to bypass these problems by treating the salts with picryl chloride in anhydrous acetone solution at ambient temperature, the conditions used by Spear to prepare picryl-5-nitrotetrazole (3) (Reference 5). This approach takes advantage of the insolubility of the alkali metal chlorides in acetone and Le Chatelier's principle to drive the reaction to completion. It also avoids the requirement for an aqueous work-up procedure. However, after 10 days there was no solid precipitate evident, and the starting materials were
NAWCWPNS TP 8188

recovered unchanged on evaporation of the acetone solutions. In a similar fashion, there was no observable reaction when a suspension of the sodium salt of the triazole 27 in a solution of picryl fluoride in anhydrous benzene was heated under reflux for 2 days; the sodium salt was reclaimed by filtration, while the picryl fluoride was reclaimed quantitatively on evaporation of the benzene solution to dryness. On the other hand, treatment of the sodium salt of 27 with picryl fluoride in dry dioxane at ambient temperature gave only sodium picrate.

As a final variant of this approach, the sodium salt of 3,5-dinitro-1,2,4-triazole (27) was treated with picryl chloride in dry acetonitrile under reflux. During the course of the reaction, brown fumes of oxides of nitrogen were evolved, and a cream-white solid was formed. From this solid was extracted 5-chloro-3-nitro-1-picryl-1,2,4-triazole (28) (previously identified by Sitzmann (Reference 20)), which was presumed to arise from the initially formed (and desired) 3,5-dinitro-1-picryl-1,2,4-triazole (7) by reaction with the sodium chloride formed simultaneously. This may be interpreted as another indication of the hydrolytic and chemical instability of 7.

\[
\begin{align*}
\text{Na} & \quad \text{PicCl} \\
\text{O}_2\text{N} & \quad \text{CH}_3\text{CN} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*}
\]

Two attempts were made to overcome this apparent chemical reactivity of the desired compound 7, each by removing the offending co-reagent chloride ion. The first was to replace the sodium salt of 25 with the silver salt, with the expectation that the chloride ion would be removed and bound up as silver chloride. The reaction of the silver salt with picryl chloride in acetonitrile under reflux did indeed give the expected precipitate of silver chloride; however, evaporation of the solvent left an unstable orange oil which evolved fumes of oxides of nitrogen. The \textsuperscript{1}H-NMR spectrum in d\textsubscript{6}-acetone indicated this material was predominantly picric acid, but small peaks between 9.4 and 9.6 could have indicated residual traces of 7. However, attempts at isolation led only to complete decomposition of that material. The second approach was to eliminate the chloride ion completely, using 1,2,3,5-tetranitrobenzene (29) in place of picryl halide. There is some precedence for this in the reaction of sodium azide with 29 and numerous derivatives to form trinitrophenyl azides (Reference 2). However, a test reaction of 29 with 4-nitroimidazole (10) in dimethylformamide solution gave only picric acid, rather than the desired 4-nitro-1-picrylimidazole (11).
Since the target compounds 6 and 7 proved inaccessible through the approach of direct coupling, two other potential routes were investigated. The first of these was an attempt at nitration of the lesser nitrated 1-picrylimida and -1,2,4-triazoles. However, these efforts were largely fruitless. Mixed nitration of 1-picrylimidazole (9) using 90% nitric acid in 96% sulfuric acid under reflux, followed by aqueous work-up, gave about 15% conversion to 4-nitro-1-picrylimidazole (11), the remainder being converted to picric acid. Less vigorous reaction conditions allowed quantitative recovery of 9, while more vigorous conditions led simply to picric acid. In a similar fashion, treatment of 11 with 90% nitric acid in 96% sulfuric acid under reflux followed by aqueous work-up allowed quantitative recovery of unreacted starting material, while more vigorous reaction conditions yielded only picric acid. 4-Nitro-1-picrylimidazole (11) was unaffected by treatment with nitronium tetrafluoroborate in sulfolane at 110°C, and was recovered in quantitative yield.

As noted above, 2-nitro-1-picrylimidazole (15) may be converted to 2,4-dinitro-1-picrylimidazole (16) by heating briefly (15 minutes) in a mixture of 90% nitric acid and 96% sulfuric acid under reflux, followed by aqueous work-up. Longer reaction times or more vigorous conditions led to formation of picric acid.
By way of contrast, attempted nitration of 1-picryl-1,2,4-triazole (22) by heating in mixed acid under reflux followed by aqueous work-up inevitably led to virtually quantitative recovery of unreacted 22. On the other hand, treatment of 22 with nitronium tetrafluoroborate gave an oily solid which included an encouraging $^1$H-NMR signal at 9.4. However, this material was also chemically unstable, decomposing with the evolution of brown fumes of oxides of nitrogen, and no identifiable product could be isolated.

The second alternative approach was applicable only to the triazoles and involved condensation of phenyl hydrazine hydrochloride (30) with dicyandiamide (31) to give 3,5-diamino-1-phenyl-1,2,4-triazole (32) (Reference 21). The intention was to diazotize 32 in the presence of excess nitrite ion to generate 3,5-dinitro-1-phenyl-1,2,4-triazole (33) in a manner analogous to the synthesis of the parent 3,5-dinitro-1,2,4-triazole (27) (References 16 and 17), but that reaction proved to be uncontrollably vigorous and no identifiable product could be isolated. However, oxidation of 32 with hydrogen peroxide in trifluoroacetic acid did afford 33 in modest yield.
However, the presence of nitro groups on the phenyl ring hinders the condensation of the hydrazine with dicyandiamide, and while the 2'- and 4'-nitrophenyldiaminotriazoles (34) and (35) may be prepared, 2,4-dinitrophenyl-hydrazine was inert to reaction with dicyandiamide. Furthermore, oxidation of 34 afforded a mixture of 5-amino-3-nitro-1-(4'-nitrophenyl)-1,2,4-triazole (36) and 1,4-dinitrobenzene (37), while oxidation of 35 resulted only in general decomposition from which no identifiable products could be identified, indicating that the triazole ring is somewhat unstable under the conditions required for oxidation of the amine functionalities.

CONCLUSIONS

A series of 1-picrylimidazoles and 1-picryl-1,2,4-triazoles have been prepared, and their physical and explosive properties have been examined. In each case the densities match reasonably well with those predicted, although they are a little low, as might be expected if the two ring systems are orthogonal. In each series the densities increase with an increasing degree of nitration. The impact sensitivity of each compound is less than that found for the 1-picrylbenzotriazoles, but there is a pronounced increase in sensitivity with increasing degree of nitration (or increasing oxygen balance), as would be expected if cleavage of a nitro group, particularly one bound to the heterocycle, is the key reaction in impact initiation. The fully substituted 1-picryl-2,4,5-trinitroimidazole and 1-picryl-3,5-dinitro-1,2,4-triazole could not be prepared. This may be due in part to the highly acidic nature of the parent heterocycles, but is also undoubtedly due to the hydrolytic instability of the materials being sought. Some evidence was seen for their transient existence, but they could not be isolated. Even if they could be isolated, extrapolation of the results obtained suggest that they would be quite sensitive explosives.
WARNING: The compounds described in this report are potentially explosives, which may be subject to accidental initiation by such environmental stimuli as impact, friction, heat or electrostatic discharge. Therefore, appropriate precautions should be taken in their handling and/or use. Melting points were determined in capillary tubes using a Met-Temp II melting point apparatus. Infrared (IR) spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer. $^1$H-NMR spectra were determined in d$_6$-acetone solutions (unless otherwise specified) using an IBM NR-80 instrument at 80 megahertz (MHz); $^{13}$C-NMR spectra were recorded on the same instrument operating at 20 MHz or on a Nicolet NT-200 instrument operating at 50 MHz. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS).

1-(2',4',6'-TRINITROPHENYL)IMIDAZOLE (9)

Imidazole (8) (0.50 g, 7.4 millimoles (mmol)) was dissolved in dimethylformamide (5 milliliters (mL)) at ambient temperature, and picryl fluoride (2-fluoro-1,3,5-trinitrobenzene (Reference 22, 1.00 g, 4.3 mmol)) was added. The solution was stirred at ambient temperature overnight and poured into water (200 mL) to give a yellow precipitate (1.08 g, 89%). Recrystallization from acetone/ethanol gave 1-(2',4',6'-trinitrophenyl)imidazole (9) (Reference 10) as yellow crystals, m.p. 200-205°C (dec). IR: 3100, 3050, 1610, 1550, 1490, 1340, 1300, 1240, 1100, 1080, 1050, 930, 905, 820, 770, 750, 720, 650 cm$^{-1}$; $^1$H-NMR: 9.26, s, H3',5'; 7.87, dd, J = 0.80 Hz, 1.30 Hz, H2; 7.40, dd, J = 1.30 Hz, 1.46 Hz, H5; 7.18, dd, J = 0.80 Hz, 1.46 Hz, H4; $^{13}$C-NMR: 148.89, C4'; 148.52, C2',6'; 138.91, C2; 131.21, C4; 130.51, C1'; 124.50, C3',5'; 122.04, C5; m/z 279 (parent ion, Cl at 280), 251, 224, and lower mass numbers.

4-NITRO-1-(2',4',6'-TRINITROPHENYL)IMIDAZOLE (11)

4-Nitroimidazole (10) (Reference 11, 0.60 g, 5.3 mmol) and picryl fluoride (Reference 22, 2.00 g, 8.6 mmol) were added to dimethylformamide (20 mL) and stirred at ambient temperature. Within 30 minutes (min) the solid was dissolved to leave a yellow solution, which was stirred at ambient temperature for 3 days and then poured into water (400 mL) to give a pale yellow solid (1.60 g, 93%). Recrystallization from acetone/ethanol gave 4-nitro-1-(2',4',6'-trinitrophenyl)imidazole (11) (Reference 10) as pale yellow needles, m.p. 281-283°C. IR: 3150, 3100, 3080, 1600, 1530,1500, 1490, 1390, 1340,1330, 1290, 1080, 1050, 970, 910, 810, 740, 710 cm$^{-1}$; $^1$H-NMR: 9.40, s, H3',5'; 8.58, d,
J = 1.54 Hz, H5; 8.11, d, J = 1.54 Hz, H2; $^{13}$C-NMR: 149.93, C4; 149.47, C4'; 148.66, C2',6'; 138.78, C2; 128.84, C1'; 125.59, C3',5'; 123.10, C5; m/z: no parent ion (Cl at 325), 249, 211, 195 and lower mass numbers.

**4,5-DINITRO-1-(2',4',6'-TRINITROPHENYL)IMIDAZOLE (13)**

4,5-Dinitroimidazole (12) (Reference 11, 1.00 g, 6.3 mmol) was dissolved in dimethylformamide (10 mL) at ambient temperature, and picryl fluoride (Reference 22, 2.00 g, 8.6 mmol) was added. The resultant solution was stirred at ambient temperature for 2 days and poured into water (400 mL) to give a pale yellow amorphous solid (2.28 g, 98%). Recrystallization from acetone/ethanol gave 4,5-dinitro-1-(2',4',6'-trinitrophenyl)imidazole (13) as pale yellow crystals, m.p. 220-223°C. IR: 3100, 3090, 3080, 1610, 1540, 1490, 1460, 1340, 1300, 1180, 1090, 920, 850, 810, 730, 720 cm$^{-1}$; $^{1}$H-NMR: 9.51, s, H3',5'; 8.41, s, H2; $^{13}$C-NMR: 149.08, C4'; 147.90, C2',6'; 143.11, C4; 138.46, C2; 132.43, C5; 126.70, C3',5'; m/z: no parent ion (Cl at 370), only peaks at much lower mass numbers.

**2-NITRO-1-(2',4',6'-TRINITROPHENYL)IMIDAZOLE (15)**

2-Nitroimidazole (14) (0.50 g, 4.4 mmol) was dissolved in dimethylformamide (15 mL) at ambient temperature, and picryl fluoride (Reference 22, 2.00 g, 8.6 mmol) was added. The resultant solution was stirred at ambient temperature for 7 days and poured into water (500 mL) to give a pale yellow solid (1.00 g, 70%). Recrystallization from ethanol gave 2-nitro-1-(2',4',6'-trinitrophenyl)imidazole (15) (Reference 10) as pale yellow needles, m.p. 196-198°C. IR: 3160, 3100, 1620, 1550, 1510, 1500, 1460, 1380, 1340, 1160, 1145, 910, 830, 815, 775, 770, 735, 720 cm$^{-1}$; $^{1}$H-NMR: 9.43, s, H3',5'; 7.81, d, J = 1.35 Hz, H5; 7.49, d, J = 1.35 Hz, H4; $^{13}$C-NMR: 149.23, C4'; 147.45, C2',6'; 146.82, C2; 131.48, C4; 130.23, C1'; 127.77, C5; 126.06, C3',5'; m/z: 324 (parent ion), 262, 236, 158, 92 (base peak).

**2,4-DINITRO-1-(2',4',6'-TRINITROPHENYL)IMIDAZOLE (16)**

**Pathway A**

2-Nitro-1-(2',4',6'-trinitrophenyl)imidazole (15) (0.40 g, 1.2 mmol) was dissolved in a mixture of 96% sulfuric acid (8 mL) and 90% nitric acid (8 mL) in an ice bath. The solution was allowed to warm to ambient temperature and was then heated to reflux for 5 min. The solution was cooled to ambient temperature and poured into ice-water (400 mL) to give a yellow solid (0.155 g, 34%).
Recrystallization from ethanol/acetone gave 2,4-dinitro-1-(2',4',6'-trinitrophenyl)imidazole (16) (Reference 10) as a yellow crystalline solid, m.p. 237-240°C. IR: 3150, 3080, 1620, 1550, 1510, 1360, 1340, 1320, 1150, 920, 850, 820, 750, 730, 720 cm⁻¹; ¹H-NMR: 9.53, s, H3',5'; 8.86, s, H5; ¹³C-NMR: 149.85, C4'; 147.09, C2',6'; 145.73, C2; 143.00, C4; 128.29, C1'; 126.93, C5; 126.89, C3',5'; m/z: no parent ion (Cl at 370), 353, 307, 278, 277 (base peak).

**Pathway B**

2,4-Dinitroimidazole (18) (Reference 12, 1.00 g, 6.3 mmol) was dissolved in dimethylformamide (20 mL) at ambient temperature, and picryl fluoride (Reference 22) (2.00 g, 8.6 mmol) was added. The resultant solution was stirred at ambient temperature for 2 days, and poured into water (500 mL) to give a pale yellow solid (1.50 g, 65%). Recrystallization from acetone/ethanol gave 2,4-dinitro-1-(2',4',6'-trinitrophenyl)imidazole (16) (Reference 10) as a pale yellow crystalline solid, m.p. 237-240°C. IR: 3150, 3080, 1620, 1550, 1510, 1360, 1340, 1320, 1150, 920, 850, 820, 750, 730, 720 cm⁻¹; ¹H-NMR: 9.53, s, H3',5'; 8.86, s, H5; ¹³C-NMR: 149.85, C4'; 147.09, C2',6'; 145.73, C2; 143.00, C4; 128.29, C1'; 126.93, C5; 126.89, C3',5'; m/z: no parent ion (Cl at 370), 353, 307, 278, 277 (base peak).

1-(2',4',6'-TRINITROPHENYL)-1,2,4-TRIAZOLE (22)

1,2,4-Triazole (21) (0.30 g, 4.3 mmol) was dissolved in dimethylformamide (3 mL) at ambient temperature, and picryl fluoride (Reference 22, 0.50 g, 2.2 mmol) was added. The resultant solution was stirred at ambient temperature for 3 days and poured into water (100 mL) to give a yellow solid. Recrystallization from acetone/ethanol gave 1-(2',4',6'-trinitrophenyl)-1,2,4-triazole (22) as pale yellow needles (0.42 g, 69%), m.p. 218-222°C. IR: 3100, 1610, 1540, 1510, 1410, 1400, 1340, 1280, 1210, 1140, 1090, 980, 960, 920, 740, 725, 670, 660 cm⁻¹; ¹H-NMR: 9.56, s, H3',5'; 8.98, s, H5; ¹³C-NMR: 154.83, C3; 148.92, C4'; 147.56, C2',6'; 147.55, C2; 143.00, C4; 128.29, C1'; 126.93, C5; 126.89, C3',5'; m/z: 280 (parent ion), 225, 167 (base peak).

3-NITRO-1-(2',4',6'-TRINITROPHENYL)-1,2,4-TRIAZOLE (25)

3-Nitro-1,2,4-triazole (24) (Reference 14, 1.00 g, 8.8 mmol) was dissolved in dimethylformamide (12 mL) at ambient temperature, and picryl fluoride (Reference 22) (2.00 g, 8.7 mmol) was added. The resultant solution was stirred at ambient temperature for 2 days, and poured into water (400 mL) to give a yellow solid (2.48 g, 88%). Recrystallization from 1,2-dichloroethane gave 3-nitro-1-(2',4',6'-trinitrophenyl)-1,2,4-triazole (25), m.p. 220-223°C.
NAWCWPNS TP 8188

(Attempted recrystallization from ethanol gave partial hydrolysis to 3-nitro-1,2,4-triazole and picric acid. Reflux in ethanol for 2 hours (h) gave complete hydrolysis, while a sample in wet acetone underwent slow hydrolysis at ambient temperature, with a half-life of ca. 7 days.) IR: 3070, 1610, 1540, 1510, 1420, 1340, 1305, 1090, 980, 920, 830, 750, 725, 715 cm⁻¹; \(^1\)H-NMR: 9.47, s, H3',5'; 9.28, s, H5; \(^{13}\)C-NMR: 164.90, C3; 150.53, C4'; 149.98, C5; 147.56, C2',6'; 128.28, C1'; 126.24, C3',5'; m/z: 325 (parent ion), 240, 224, 167, plus lower mass numbers.

3,5-DINITRO-1-PHENYL-1,2,4-TRIAZOLE (33)

Hydrogen peroxide (90%, 3.2 mL) was added to trifluoroacetic acid (4.5 mL) at 0°C, and 3,5-diamino-1-phenyl-1,2,4-triazole (32) (Reference 21, 0.75 g, 4.4 mmol) was added at 0-10°C. The orange solution was allowed to warm to ambient temperature and was then warmed to 70°C for 4 h. The solution was cooled and then evaporated to dryness, and the residue was purified by chromatography (silica/dichloromethane) to give a solid (0.15 g, 15%). Recrystallization from cyclohexane gave 3,5-dinitro-1-phenyl-1,2,4-triazole (33) as pale yellow crystals, m.p. 98-99°C. IR: 1575, 1560, 1510, 1415, 1335, 1310, 850, 830, 765, 690 cm⁻¹; \(^1\)H-NMR: 7.90-7.60 m; \(^{13}\)C-NMR: 159.61, C3; 151.50, C5; 137.60, C1'; 132.29, C4'; 130.42, C3',5'; 126.98, C2',6'; m/z: 235 (parent ion), 207, 182, 159, 143, 131, 107, 91 (base peak), 77.

3,5-DIAMINO-1-(2'-NITROPHENYL)-1,2,4-TRIAZOLE (34)

2-Nitrophenylhydrazine hydrochloride (2.50 g, 13.2 mmol) and dicyandiamide (1.50 g, 17.9 mmol) were added to water (20 mL) and heated under reflux for 1 h, giving an intensely colored red/purple solution. Filtration followed by basification with 2N sodium hydroxide resulted in the formation of dark, permanganate-like crystals (1.56 g, 54%) identified as 3,5-diamino-1-(2'-nitrophényl)-1,2,4-triazole (34), m.p. 170-72°C. IR: 3300-3400 (very broad), 1600, 1530, 1490, 1400, 1325, 1240,1200, 1130, 1020, 730 cm⁻¹; \(^1\)H-NMR: 8.00, m, 1H; 7.38, m, 1H; 6.63, m, 2H; \(^{13}\)C-NMR: 162.41, C3; 159.35, C5; 145.16, C2'; 136.57, C5'; 130.48, C1'; 126.47, C4'; 116.27, C3'; 115.58, C6'; m/z: 220 (parent ion and base peak),136, 135, 107, 77.
3,5-DIAMINO-1-(4'-NITROPHENYL)-1,2,4-TRIAZOLE (35)

4-Nitrophenylhydrazine hydrochloride (0.75 g, 4.0 mmol) and dicyandiamide (0.45 g, 5.4 mmol) were heated in water (10 mL) under reflux for 3 h to give a dark red solution, which yielded a brick-red solid in a yellow solution. Cooling and filtration gave a brick-red solid (0.54 g, 62%) identified as 3,5-diamino-1-(4'-nitrophenyl)-1,2,4-triazole (35), m.p. 306-308°C (dec.). IR: 3440, 3310, 1630, 1600, 1550, 1500, 1460, 1330, 1080, 750 cm\(^{-1}\); \(^1\)H-NMR: 8.26, d, H\(_{3',5'}\); 7.74, d, H\(_{2',4'}\); 6.60, NH\(_2\); 5.38, NH\(_2\); \(^1\)C-NMR: 161.98, C3; 154.73, C5; 143.14, C4'; 142.85, C1'; 124.92, C3',5'; 119.74, C2',6'.

OXIDATION OF 3,5-DIAMINO-1-(4'-NITROPHENYL)-1,2,4-TRIAZOLE (35)

Hydrogen peroxide (85%, 1.5 mL) was added to trifluoroacetic acid (3 mL) at 0°C, and 3,5-diamino-1-(4'-nitrophenyl)-1,2,4-triazole (35) (0.50 g, 2.3 mmol) was added slowly at that temperature. The solution was then allowed to warm slowly to ambient temperature and was then heated to 70°C for 1 h. Cooling overnight gave a fine white precipitate (0.050 g, 9%), m.p. 278-280°C (dec.), tentatively identified as 5-amino-3-nitro-1-(4'-nitrophenyl)-1,2,4-triazole (36). IR: 3400, 3300, 3150, 1650, 1520, 1360, 860, 750 cm\(^{-1}\); \(^1\)H-NMR: 8.41, d, H\(_{3',5'}\); 7.90 d, H\(_{2',6'}\); 7.52, NH\(_2\); \(^1\)C-NMR: 160.60, C3; 156.03, C5; 146.56, C1'; 140.67, C4'; 125.07, C3',5'; 124.57, C2',6'; m/z: 250 (parent ion), 150, 122 (base peak). The filtrate was evaporated to dryness to leave a foamy solid. Flash chromatography (silica/chloroform) gave only one product, a tan solid (0.03 g, 8%), m.p. 173°C, identified by IR, \(^1\)H-NMR, and m/z as p-dinitrobenzene.
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