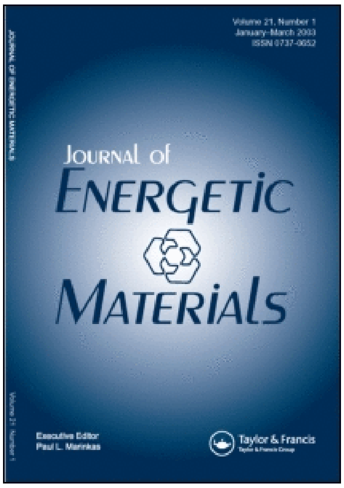

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Explosive desensitization studies via chemical group modification II. 3,5-diamino- and 3,5-dichloro-2,4,6-trinitrotoluene(1)

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NOTES:

EXPLOSIVE DESENSITIZATION STUDIES VIA CHEMICAL GROUP MODIFICATION II. 3,5-DIAMINO- AND 3,5-DICHLORO-2,4,6-TRINITROTOLUENE(1)

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ABSTRACT

TNT molecule is significantly desensitized by substitution of ring hydrogens by $-NH_2$ and -Cl functions. Calculated CJ pressures and detonation velocities for mono- and diamino-TNT show that their performance would be better than that of TNT.

INTRODUCTION

Sensitivity of a solid explosive to initiation of detonation can be thought of as a combination of two parts, namely, molecular and crystalline. The molecular part conceivably arises from the inherent property of the molecule (i.e., instability) and the crystalline part from the relative force with which the molecules are held together (intermolecular forces). Molecular sensitivity of an explosive is thus a function of its molecular chemical structure. By altering this structure, one should be able to modify the sensitivity.

Kamlet, et al(2), have shown that for each chemically similar class of C,H,N,O organic explosives (i.e., nitroaliphatics, nitroaromatics, etc.) an empirical relationship exists between impact heights (see Experimental) and the chemical structure (i.e., the relative number of C,H,N and O atoms and thus the oxygen balance). It is also postulated that a "trigger linkage" exists in each explosive molecule which undergoes breakage upon delivery of the impact stimulus. Presumably, the trigger linkage is the weakest bond in the molecule.

Investigations of structure-sensitivity relationships could lead to understanding of the molecular mechanisms of initiation (or ignition) of energetic materials as well as the chemical factors contributing toward such processes. An understanding of initiation mechanisms is very valuable toward controlling the sensitivity of tailor-made explosive formulations for munitions. In order to increase the survivability of a weapon, it is important to be able to desensitize the explosive as it is often the most vulnerable component.

Desensitization studies of RDX and TNT via molecular level chemical modification were carried out in this laboratory(1). As a rationale and background of the chemical modification approach, a relationship between the sensitivities of TNB and amino substituted TNB's (picramide, DATB, TATB) can be cited. In this series, TNB gets progressively desensitized by successive substitution of ring hydrogens by $-NH_2$ groups. Similarly, it should be possible to effectively desensitize the TNT molecule by amino-substitution of its ring hydrogens. In fact, mono- and diamino-derivatives of TNT were synthesized and tested during the course of this work and were found to be dramatically less sensitive than TNT. In addition, as shown from studies with dichloro-TNT, chlorine substitution was also found to cause marked desensitization. The aim of this paper is to report the synthesis and testing of dichloro- and diamino-derivatives of TNT.

EXPERIMENTAL

Synthesis

Monoamino-TNT was synthesized by two procedures. One was already discussed(1). The second procedure, starting from 3-chloro toluene, is described below (Scheme A). Dichloro and diamino derivatives of TNT(3) were synthesized from 3,5-dichloro toluene via Scheme B.

DSC Runs

These were accomplished using a Perkin-Elmer Differential Scanning Calorimeter Model 1; one to three mg samples were used.

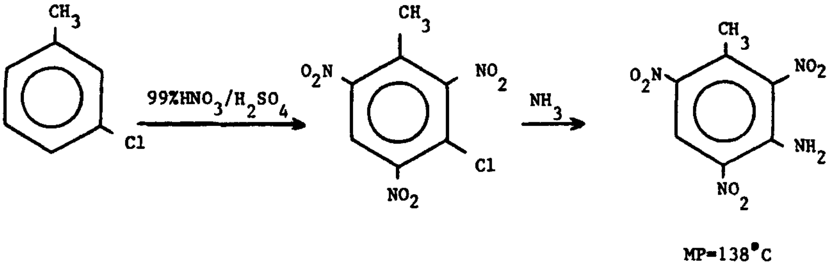
Impact Sensitivity Measurements

For these measurements, the Picatinny Arsenal impact machine was used. With a 2.5 kg drop weight (Type 12 tool, sample on sand paper)(4), the height of fall in centimeters which produces explosions in 50% of the samples tested is the reported impact sensitivity index. The procedure used to determine the 50% point was the Bruceton up-and-down method(4).

RESULTS AND DISCUSSION

Measured sensitivities and thermal data (DSC) of amino- and dichloro-derivatives of TNT are shown in Table 1. The impact sensitivity values in Table 1 show that amino and chloro substitution of the ring hydrogens in TNT causes a significant (by several factors) desensitization of the explosive molecule. Also, the DSC peak maximum values show that the amino-substituted molecules are thermally stabilized as well. The thermal stability of 3,5-dichloro-TNT is higher than that of 3,5-diamino-TNT showing that chlorine atoms confer even greater thermal stability than the $-NH_2$ groups.

SCHEME A



SCHEME B

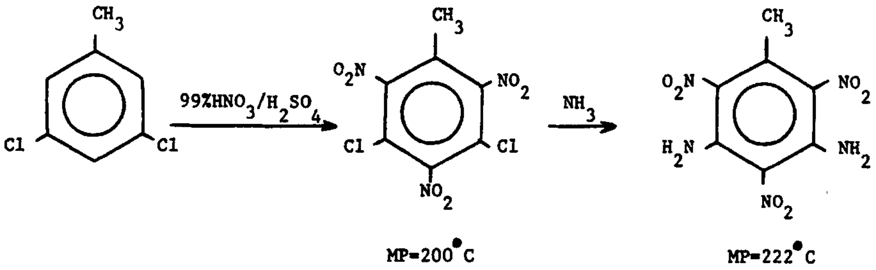


Table 1. Impact and DSC Data

Compound	50% Impact Ht. (cm)	DSC Chemical Reaction Exotherm Peak Max (°C)
TNT	61 ± 2	325
3-Amino-TNT	174 ± 6	335
3,5-Diamino-TNT	239 ± 0.4	345
3,5-Dichloro-TNT	202 ± 2	380

Performance Calculations

Theoretical detonation pressures (CJ-pressures) and velocities for amino derivatives of TNT were calculated using the TIGER Code (BKWR-thermo-hydrodynamic equation of state calculations)(5) and these are compared in Table 2 with the measured value for TNT. Theoretical maximum densities (TMD) and heats of formation which were required for these calculations were estimated (see Appendix). The data in Table 2 show that the detonation performance of the amino-substituted TNT molecules is better than that of TNT.

Table 2. Performance Data for Amino-Derivatives of TNT

Compound	Density (g/cm^3)	Detonation Velocity (mm/μs)	CJ Pressure (kbars)
TNT	1.64[a]	6.942	189
Monoamino-TNT	1.72[b]	7.444	222
Diamino-TNT	1.80[b]	7.780	250

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[a] Theoretical Max Density (TMD) of TNT: 1.65 g/cm^3(6). The above experimental value is at 99.4% TMD.

[b] Theoretical Max Density

Mechanism of Desensitization by Amino-Groups and Chlorine Atoms

Perhaps the reactive site in TNT is the methyl group. There are experimental results described below which point out toward that possibility. Thus, previous work in this laboratory(7) has shown that TNT could be sensitized by proton abstractors and hydrogen atom abstractors (e.g., benzoquinone, lead tetraethyl) which act on the methyl group. In the case of proton abstractors, the TNT anion (with a $-CH_2^-$ group) seems to be the responsible species, and in the case of hydrogen atom abstractors, it is the 2,4,6-trinitrobenzyl radical (with a $-\dot{C}H_2$ group). The electronic absorption spectra of both the anion and the free radical have been determined by light excitation of the explosive (TNT) and time-resolved spectroscopy of the resulting transient species (anion in polar solvents and the free radical in gas phase). In TNT, strong electron withdrawing nitro-groups weaken the CH bond of the methyl group and facilitate its rupture. Conversely, when electron donating groups like $-NH_2$ and -Cl are introduced, they probably produce a reverse effect by strengthening the C-H bond, thereby desensitizing the explosive molecule.

This mechanism is further substantiated by recent other work(8) showing that this C-H bond rupture is a very likely rate determining step in TNT initiation.

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APPENDIX

Estimation of TMD and ΔH_f (Heat of Formation) for Amino-Derivatives of TNT

The following table contains the TMD's and ΔH_f's of TNB and its amino-derivatives.

Table A-1. Increment in TMD and ΔH_f Relative to Immediate Predecessor

Compound	TMD[a] (g/cm^3)	Increment in TMD from its Previous Member	ΔH_f[a] (kcal/mole)	Increment in ΔH_f from its Previous Member
TNB	1.69		-11.40	
Picramide	1.76	0.07	-20.07	-8.67
DATB	1.84	0.08	-29.23	-9.16
TATB	1.94	0.10	-36.85	-7.62

[a] Donna Price and Harold Hurwitz, NOLTR 63-216, U.S. Naval Ordnance Laboratory, White Oak, MD, November 1963.

Assuming that the increments from member to member in TMD (in column 3 above) and in ΔH_f (in column 5) is constant in both TNB and TNT series (a valid assumption since these increments in both series arise from the same cause, viz., amino-substituion of ring hydrogens), the values for amino-derivatives of TNT are calculated thus.

Table A-2. Calculated TMD and ΔH_f Values for Amino-Derivatives of TNT

Compound	TMD (g/cm^3)	ΔH_f (kcal/mole)
TNT	1.65[b]	-17.81[a]
Mono-Amino-TNT	1.65 + 0.07 = 1.72	-17.81 - 8.67 = -26.48
Diamino-TNT	1.72 + 0.08 = 1.80	-26.48 - 9.16 = -35.64

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[a] Same as a above
[b] Reference 6