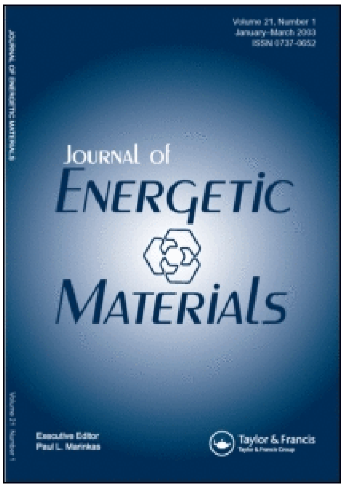

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Thermal behavior and detonation properties of d3-hexanitrotrishomocubane

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RESEARCH NOTE

THERMAL BEHAVIOR AND DETONATION PROPERTIES OF D3-HEXANITROTRISHOMOCUBANE

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ABSTRACT

The DSC thermogram of the title compound (1) reveals the following characteristics: When a 3.34 mg sample of 1 was heated at 10 $^{o}C\text{-}min^{-1}$, exotherm onset occurred at 272 ^{o}C, reached a maximum at 308 ^{o}C, and subsided at 331 ^{o}C. A second smaller exotherm was initiated at 331 ^{o}C, reached a maximum at 338 ^{o}C, and subsided at 355 ^{o}C. A study of the shock sensitivity of 1 as measured by the exploding foil slapper technique revealed that 1 is less shock-sensitive than TNT. Explosive output calculations show that it is a substantially more powerful explosive than is TNT.

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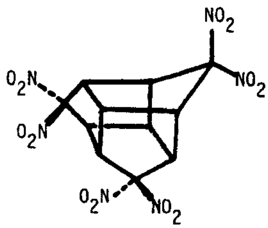
INTRODUCTION

There is considerable current interest in the synthesis[1-7] and thermal characterization[8] of polynitropolycyclic "cage" molecules. Compounds of this type, particularly those that are relatively highly strained and that contain several NO_2 groups as substituents, are predicted on the basis of thermohydrodynamic considerations to comprise a new class of high-density energetic materials.[9,10]

As part of a program involved with the synthesis of polynitropolycyclic cage compounds, 4,4,7,7,11,11-hexanitropentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane ("D_3-hexanitrotrishomocubane", **1**) has been synthesized recently.[11]



1

The following values have been calculated for **1**:[12] density = 1.84 g-cm^{-3}; ΔH_f = -36.44 kcal/mol; strain energy = 44.6 kcal/mol; detonation pressure = 283.8 Kbar; detonation velocity = 7.95 km/sec. We now report the results of a study of the thermal behavior and detonation properties of **1**.

EXPERIMENTAL

Differential scanning calorimetry data was obtained by using a Perkin-Elmer DSC-4/TADS system equipped with a System 4 Microprocessor Controller. The system was operated in the heating mode at a sensitivity of 2 mcal-s^{-1} at full-scale deflection. The heating rate for all runs was 10 ^{o}C-min^{-1}. The sample of **1** (3.34 mg) was contained in a high pressure, gold plated stainless steel capsule capable of sustaining an internal pressure up to 150 bar (2,175 psig).

The shock sensitivity of **1** was measured by using the exploding foil slapper technique.[13,14] The apparatus used in this technique provides a 2 mil mylar disc that is driven by an aluminum plasma created by applying 12 kV across two electrodes which contain the aluminum foil. The mylar disc is propelled through a barrel; when it impacts upon the target (**1**), a precise level of shock intensity results that initiates the explosive process. The target is placed at the center of a confinement disc. After detonation, the chamber in which the target had been confined becomes tapered, and a dent is recorded in an aluminum witness plate. The initial and final taper diameters provide a measure of explosive sensitivity.

RESULTS AND DISCUSSION

Thermal Behavior of 1.

The DSC thermogram obtained for a 3.34 mg sample of **1** heated at 10 ^{o}C-min^{-1} is shown in Figure 1 (solid line). The onset of an exothermic reaction occurred when the temperature reached 272 ^{o}C. The exotherm maximum occured at 308 ^{o}C, and the exothermic process ended when the temperature reached 331 ^{o}C. A second smaller exotherm then set in at 331 ^{o}C, reached a maximum at 338 ^{o}C, and subsided at 355 ^{o}C. The dotted line in Figure 1 shows the corresponding DSC curve obtained for TNT that had been normalized by sample weight.

Results of Shock Sensitivity Tests on 1.

The shock sensitivity data that were obtained for **1** are summarized in Table 1 and related to a TNT reference:

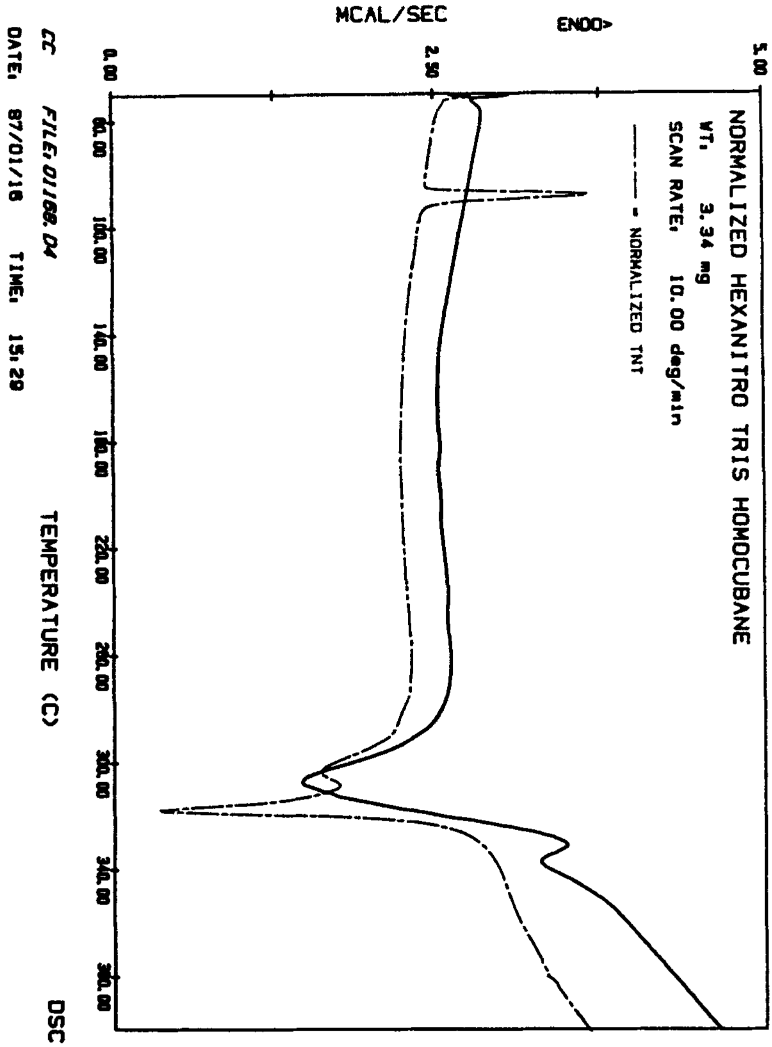


FIGURE 1

DSC Curves: For 1 (Solid Line) and for Normalized TNT (Broken Line).

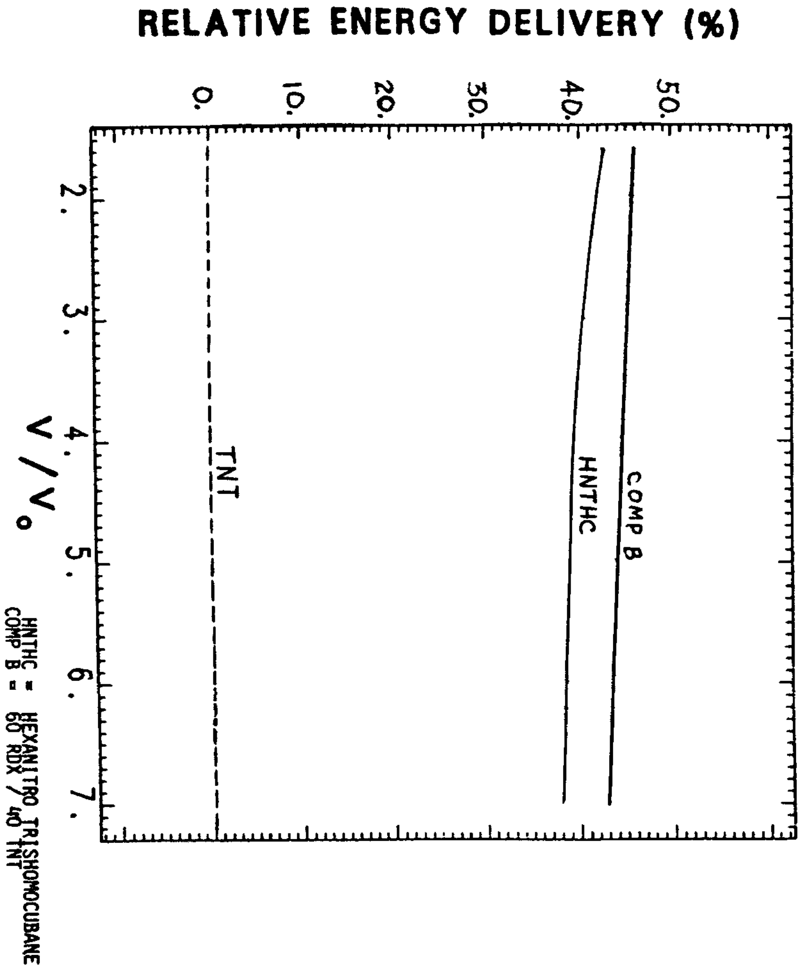


FIGURE 2

Plot of Relative Energy Delivery (%) vs. V/V_0 for Comp B, 1 and TNT.

TABLE 1

Results of Shock Sensitivity Tests for **1** and for TNT.[a]

Compound	Sample Weight (mg)	Taper Diameter (in.) Initial	Final	Taper Angle (Degrees)[b]
TNT	36.4	0.153	0.165	3.9
TNT	36.8	0.153	0.167	4.4
TNT	37.1	0.154	0.167	4.1
1	38.1	0.145	0.154	2.9

[a] A constant stimulating voltage of 12 kV was employed.

[b] The taper angle is defined as the angle which the inclined face of the taper makes with the vertical.

Inspection of the data in Table 1 reveals that detonation of **1** produces smaller initial and final taper diameters than does detonation of TNT when the same stimulus is applied to either sample. This result indicates that **1** is less shock-sensitive than is TNT. In addition, detonation of **1** also produces a smaller taper angle than does detonation of TNT; hence, the propagation rate is slower in **1** than in TNT.

Since only ca. 50 mg of **1** was available for testing, maximum steady state detonation conditions could not be achieved. Accordingly, no attempt was made to estimate explosion output. Nevertheless, it is instructive to compare the calculated explosive output of **1** to a standard explosive (e.g., TNT). A plot of relative energy delivery vs. V/V_0 is shown in Figure 2. Here, "relative energy delivery" is defined as the percent energy difference between the isentropic expansion of the gaseous products of an explosive and that of TNT. V/V_0 is the ratio of the specific volume of the gaseous products to that of the intact explosive. The plot in Figure 2 indicates that the calculated energy output of **1** is at most 5% below that of "Comp B", (i.e., an explosive mixture composed of 60% RDX and 40% TNT). It is evident from inspection of Figure 2 that both Comp B and **1** are substantially more powerful explosives than is TNT.

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