

# **THERMAL INVESTIGATION OF THE CRYSTALLISATION NUCLEANT FORMED BETWEEN 2,4,6 TRINITROTOLUENE, (TNT) AND 2,2',4,4',6,6' HEXANITROSTILBENE (HNS)**

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## **Abstract**

Hexanitrostilbene (HNS), is added to trinitrotoluene (TNT), in order to improve the grain structure of cast munitions. The formation and composition of the nucleant material has been investigated by thermal methods using mixtures of HNS and TNT, with composition in the range 0.5%, the normal casting level, to 50% w/w HNS to TNT. These were cycled between ambient and upper temperatures in the range 160 to 235°C. Endotherms in the DSC traces, due to nucleant decomposition, have been observed in situ without the need for separation and purification. DSC enthalpy measurements, before and after thermal decomposition, were used to determine the composition of separated nucleant. Nucleant regeneration after decomposition, was investigated by thermal methods. Nucleant could not be recrystallised from solvents. Results have been interpreted on the basis of the formation of a solid solution of TNT in HNS, rather than a complex of formula TNT<sub>2</sub>HNS.

**Keywords:** crystallisation, DSC, hexanitrostilbene (HNS), trinitrotoluene (TNT)

## **Introduction**

Low impact sensitivity, low melting point, low melt viscosity and low production costs are responsible for the extensive use of TNT in high explosive warheads, either as a high explosive composition or, an energetic binder for other high explosive compounds. High melting point explosives, such as 1,3,5-trinitro-1,3,5-triazacyclohexane, (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane, (HMX) can be effectively melt cast, when mixed with low melting TNT, at safe working temperatures using steam heating. During setting TNT undergoes a 12% volume contraction,  $\rho_{\text{liquid}} 1.47 \text{ g}\cdot\text{cm}^{-3}$   $\rho_{\text{solid}} 1.65 \text{ g}\cdot\text{cm}^{-3}$  [1], which can be overcome either by biscuit filling techniques [2] or by the use of a molten TNT header above the munition filling aperture with slow cooling

[3]. In some castings, TNT is susceptible to large crystal growth (irreversible expansion) during thermal cycling [4]. TNT exists in two primary crystal structures, monoclinic or orthorhombic [5, 6]. Both crystal forms are obtained by recrystallisation from solvents or the molten phase under controlled conditions. When heated, the orthorhombic structure is reported to change into the monoclinic form at or just before the melting point [7, 8].

Although TNT melts at 80.7°C it can set as low as 60°C. Growth of crystals from the supercooled liquid is very rapid resulting in the formation of highly orientated columnar crystals with the long axis parallel to the direction of the major heat loss, generally normal to the sides of the shell casing. Needle shaped crystals are undesirable since they are particularly prone to irreversible expansion during thermal cycling [4] and exhibit anisotropic thermal properties. The linear thermal expansion coefficient in the shorter 'b' axial direction, normal to the principal needle axis, is a factor of four greater than the coefficients in the crystallographic 'a' and 'c' directions [9]. As a result, during thermal cycling the needles will tend to separate increasing voids between them and increasing internal stresses within the needles. Methods of overcoming these problems have been the subject of a number of investigations [1, 4, 10–15]. Rapid stirring of the melt as it cools can reduce the thermal gradient across the filling and produce a creamed material [16], or addition of finely ground TNT crystals to the melt, at the normal setting temperature, immediately prior to setting, can reduce the supercooling and improve the randomness of the filling. The most successful process involves adding trace amounts (0.3–0.5%) of the sparingly soluble material hexanitrostilbene (HNS) to the mixture. HNS produces the optimum number of nucleating sites following thermal cycling according to the Bofors patent [17]. (TNT is heated to 110°C, until the small amount of added HNS is completely dissolved, when the mixture is cooled until set, normally about 74°C. Reheating above the melting point, but less than 85°C, followed by casting produces the necessary texture in the filling.) The second heating cycle is required to produce the optimum filling texture since the material still exhibits supercooling at the end of the first heating cycle. This nucleant process eliminates supercooling, improves grain structure orientation and improves the filling's mechanical properties [12, 13]. Repeated heat cycling through the molten state does not destroy the fine grain texture providing the temperature does not exceed 85°C. If the temperature exceeds 90°C the nucleant is destroyed.

A complex of TNT and HNS in the ratio of 2:1 has been proposed as the effective nucleant [10–12]. This nucleant was not observed during the first heating cycle, but formed as the TNT began to melt during the reheat cycle. The thermal stability of the nucleant appears to depend on the environment during the experiment. DSC and optical microscopy studies on enriched nucleant indicate that the complex is decomposed above 85°C and less than 100°C and is not reformed by further heating cycles regardless of temperature [12]. Hot stage mi-

crosscopy on the normal TNT with 0.5% HNS indicates that if the sample is heated to between 85 and 100°C the texture is lost but can be regained by heating above the decomposition temperature 115°C and repeating the Bofors cycle [13]. During nucleant decomposition, TNT appeared to be melting away from the complex and appearing on the surface. The nucleant is different from either TNT or HNS. The nature of the nucleant its structure, thermal stability and the conditions under which it is formed are uncertain. This study was undertaken to identify the formation process and to examine the nucleant properties. Attempts would be made to prepare samples of the 'complex' by precipitation from solutions in selected organic solvents.

## Experimental

### *Materials*

TNT and HNS were supplied by the explosives and special products division Royal Ordnance, Bridgewater. All other chemical reagents and solvents used were 'Analar' or 'Spectrol' grade materials supplied by B.D.H. (Merck) Ltd. of Poole, Dorset, UK. TNT was purified by the method of Gey, Dalby and Van Dolah [18] and recrystallised from methanol to produce the monoclinic form, whilst ethanol was used to produce the orthorhombic form. All samples were vacuum dried at 20°C and  $10^{-2}$  mm Hg for 48 h before use. HNS was purified by recrystallisation from either dimethylformamide (DMF) or N-Methylpyrrolid-2-one (NMP) using toluene to assist precipitation. Filtered solids were washed with methanol and vacuum dried as described above before use.

Purity of materials was confirmed by high performance liquid chromatography (HPLC) using an LDC Milton Roy CM 4000 system fitted with an ODS 2 column supplied by Jones Chromatography Ltd. Methanolic solutions of TNT were injected onto the column and eluted with a 60 /40 methanol/ distilled water mobile phase. HNS, in acetonitrile solution, was analysed using a 52.5 /47.5 acetonitrile/ distilled water mobile phase. Purified samples of TNT and HNS were found to be >99.9% pure. Purified HNS showed no evidence of hexanitrobibenzyl (HNBB) the normal impurity [19].

### *Nucleant preparation and purification*

#### a) Melt processes

Preparation of the purified nucleant was undertaken by modifications of literature methods i.e hot filtration and vacuum sublimation [11, 13]. 10 g samples of TNT containing 0.5% HNS were subjected to the standard Bofors cycle followed by remelting at 85°C in the apparatus shown in Fig. 1, using the more

even heating of circulating hot oil, rather than radiant heating employed in earlier methods. Other nucleant samples were prepared by heating 10 g samples of 3% HNS mixtures to 160°C, until the HNS dissolved, cooling to 85°C and, after 10 min at that temperature, filtering off the precipitated solid on the sintered glass frit, porosity 3, leaving the liquid phase in the flask for further use.

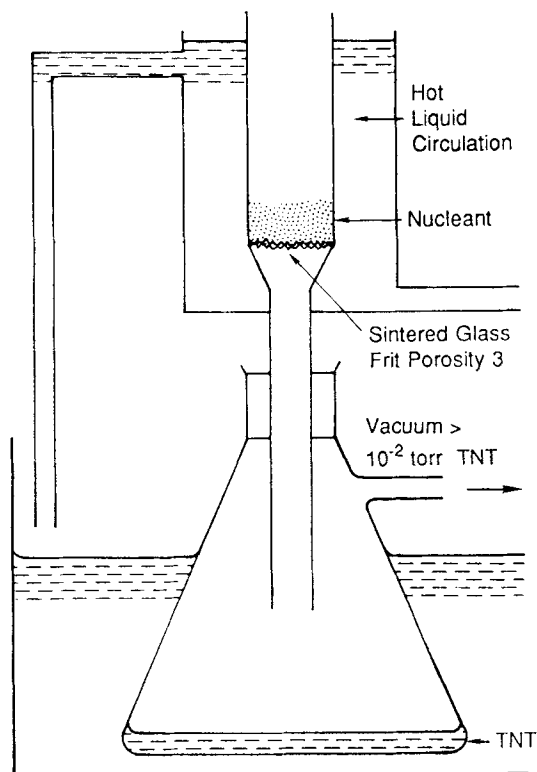


Fig. 1 Apparatus for hot filtration of nucleant from molten TNT

Preliminary DSC measurements indicated appreciable TNT contamination and hence the nucleant was purified by vacuum sublimation. Bulked samples of filtered nucleant were subjected to vacuum sublimation at 75°C and 10<sup>-2</sup> mm Hg using liquid nitrogen as the condensing agent in the cold finger, until no further material collected on the cold finger. The sublimation process was repeated until the DSC trace showed no evidence of the TNT melting endotherm.

#### (b) Solvent methods

Saturated solutions of HNS in a range of solvents were prepared at or near the solvents' boiling points. The solutions were then treated with two mass

equivalents of TNT and slowly cooled to room temperature. Solids separating out were filtered off, vacuum dried overnight,  $10^{-2}$  mm Hg  $20^{\circ}\text{C}$  and identified by their thermal properties using DSC measurements. The experiment was repeated using solutions saturated with TNT and HNS, also at the boiling point. Any solids separating on cooling to room temperature were identified as described above.

### *Equipment*

DSC experiments were performed on a Mettler TA 4000 system with a DSC 30 chamber connected to a TC 11 TA Processor. Output was to an Epson FX-850 printer. Alumina in a sealed aluminium crucible or an empty crucible was used as the reference material.

Differential thermal analysis was performed on Stanton – Redcroft STA-780 DTA connected to a GOULD BS-273 chart recorder, and the results obtained were used to confirm some of the results obtained by DSC. Alumina was the inert reference material.

### *Thermal analysis experiments*

DSC experiments used 10–30 mg samples prepared from dry mixtures of TNT and HNS, in the composition range 0.5%, the normal casting concentration, to 50% w/w HNS to TNT. Samples were repeat cycled at  $5\text{ deg}\cdot\text{min}^{-1}$  in an atmosphere of dry nitrogen between ambient and upper temperatures in the range  $160$  to  $235^{\circ}\text{C}$  as detailed in the table below.

Since only a single heating rate could be programmed on the instrument at any time  $5\text{ deg}\cdot\text{min}^{-1}$  was chosen as the compromise between speed and maximum information for both heating and cooling cycles. For sample masses less than 15 mg, the thermal properties of the sample were obscured by the low signal to noise ratio and the non-linear base line. It was anticipated that the extra solubility of HNS in TNT at higher temperatures, around  $170^{\circ}\text{C}$ , would provide both information on the phase diagram for the mixture and also yield higher concentrations of the effective nucleant thus enabling the properties of the nucleant to be measured during formation and not separated out from the mother liquor as in previous studies. Samples of the nucleant at various stages of the purification process were studied by DSC and the proportions of TNT and HNS in the nucleant estimated from the relative areas of the endotherms.

## **Results and discussion**

DSC traces for pure TNT heated, at  $5\text{ deg}\cdot\text{min}^{-1}$ , between  $25$  and  $175^{\circ}\text{C}$  showed a consistent melting endotherm on a slowly curving baseline. During

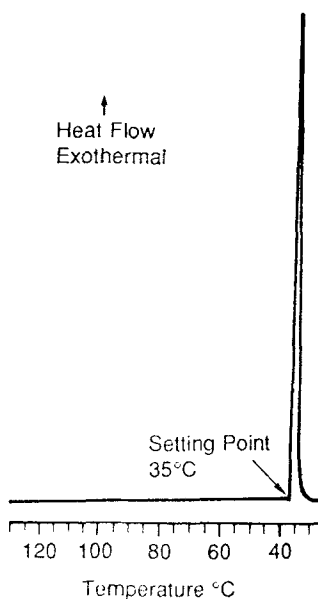
Table 1 DSC experiments on TNT/HNS mixtures

% HNS (w/w)	0	0.5	1.0	3.0	5.0	7.0	10.0	15.0	20.0
Upper cycle temperature °C	(1) 175 (2) 200 (3)	100 85	175	175 225	160 175 220	175 225	175 225	175 235	175 235
No. of thermal cycles	(1') 1 (2') 1 (3')	1 1	3	2 2	2 2 3	3 2	3 3	3 3	2 2

## Notes for Table

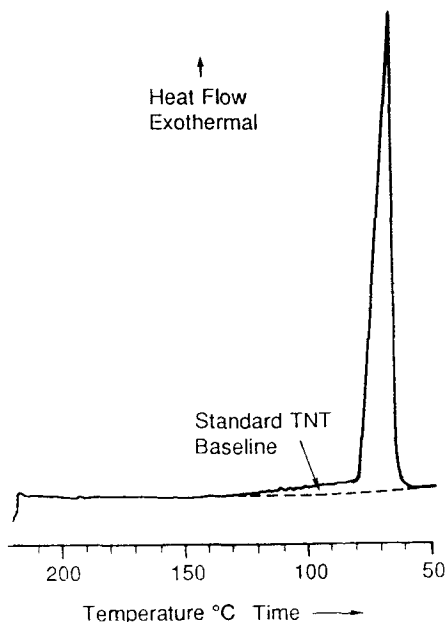
Sample cycled from ambient 20°C to the upper temperatures given in line 1 for the number of cycles given in line 1' and then cycled to higher temperatures lines 2 and 3 for the number of cycles in line 2' and 3'.

successive cooling cycles severe supercooling was observed, with setting occurring just before the commencement of the next heating cycle. HNS impurity, above the 0.5% level, reduced the supercooling during setting to undetectable levels after the first heat cycle provided the temperature did not exceed 160°C. Samples with less than 1% HNS, cycled above 200°C, showed similar setting point reductions to pure TNT samples (Fig. 2). This may indicate incorrect nucleant formation or interference with the setting process arising from the decomposition reaction discussed later. The setting range for the HNS treated samples increased compared to the pure material. Solubility of HNS in liquid TNT increased with temperature from 0.2% at 85°C to ~5% at about 200°C. All powdered samples, except the separated nucleant, had to be thermally cycled once to form the nucleant.



**Fig. 2** Partial cooling curve showing extreme supercooling for a 1% HNS sample previously heated to 200°C at 5 deg·min<sup>-1</sup>

Cooling of samples containing between 3 and 10% HNS from above 160°C produced an exothermic curvature in the base line below 130°C prior to the TNT setting exothermic (Fig. 3). This was a distinct deviation from the pure material baseline, indicated by the dotted line on the figure and could be due to the precipitation of excess solid HNS, nucleant or, most probably, a mixture of both. Optical microscopy [20] has indicated that small fine particles of solid are being precipitated during this part of the cycle. Baseline deviation appears to be at a maximum between 3 and 5% HNS suggesting a dependence on the concentrations of both TNT and HNS. These observations indicate that the effective



**Fig. 3** DSC cooling curve at  $5 \text{ deg}\cdot\text{min}^{-1}$  for a sample at TNT with 5% HNS previously heated from 40 to  $220^\circ\text{C}$  at  $5 \text{ deg}\cdot\text{min}^{-1}$

nucleant is HNS containing some TNT as it precipitates from the molten TNT solution. Because of the small change in slope, the DSC software could not identify a clear onset temperature for this effect. Inspection of the trace suggests an onset temperature of around  $135^\circ\text{C}$ .

Samples containing between 3 and 5% HNS, which had been previously heated to  $>160^\circ\text{C}$  and exhibited the exothermic curvature prior to the TNT setting point during the cooling cycle, exhibited during subsequent heating cycles, after the normal TNT melting endotherm, an endothermic deviation starting at about  $105^\circ\text{C}$  and finishing at about  $115^\circ\text{C}$  (Fig. 4). If the samples were heated to  $200^\circ\text{C}$ , then this deviation became a definite endothermic peak, which corresponded to previously reported dissociation of the nucleant. After the first heating cycle the peak was a consistent feature: the third cycle trace was identical with that shown in the figure. Identical results were obtained with four samples, with the same composition, subjected to the same thermal treatment. Nucleant regeneration, after thermal dissociation at temperatures  $>90^\circ\text{C}$ , by heating to  $120^\circ\text{C}$  only occurs at concentrations of HNS above 0.5% when some of the material starts to precipitate from solution well above the setting point of TNT. The endotherm occurring between 105 and  $120^\circ\text{C}$  for the samples containing 3 to 5% HNS is in agreement with the enriched nucleant studies and could be TNT trapped in the HNS lattice melting out as the nucleant decomposes leaving solid



HNS dispersed in molten TNT. Development of this peak appears to correspond to the solubility of the HNS in TNT. These deviations were not observed with samples whose HNS concentrations were outside the range 3 to 7% HNS. Below 3% there is insufficient HNS precipitating to produce a significant deviation and above 7% there is insufficient TNT to dissolve the HNS and hence there will be a reduced amount of precipitate formed during the cooling process. If less than a 15 mg sample was used, these deviations were difficult to observe, probably due to the limited quantity of nucleant present.

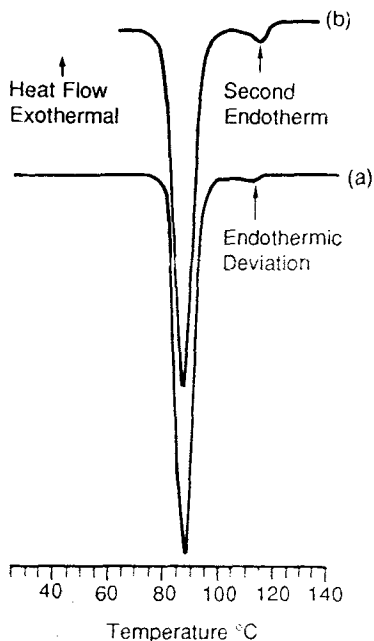


Fig. 4 DSC heating curve for sample of TNT +5% HNS after thermal cycling; (a) 20 to 160 to 40°C at 5 deg·min<sup>-1</sup>; (b) 20 to 200 to 40°C at 5 deg·min<sup>-1</sup>

Earlier studies showed that the most effective nucleant was observed only in systems in which the HNS has been dissolved at higher temperatures, i.e. the Bofors type cycle. The supercooling observed during the first heating cycle for the 0.5% HNS samples could be nucleant formation as the HNS crystallised out, which is then effective during further cycles. Excess HNS, which did not dissolve in the TNT at the higher temperature, was separated off and has been shown to be a less effective nucleant than material which dissolved and recrystallised [20].

Repeat cycling to 220°C of samples with >5% HNS concentrations produced an exothermic deviation in the baseline above 190°C (Fig. 5). Similarly, when these samples were cooled from above 200°C, they exhibited a broad exother-

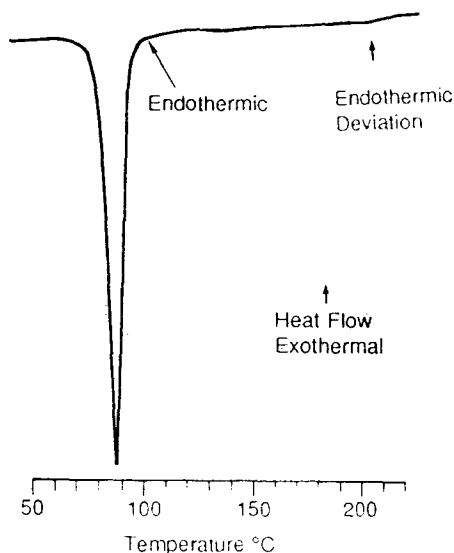
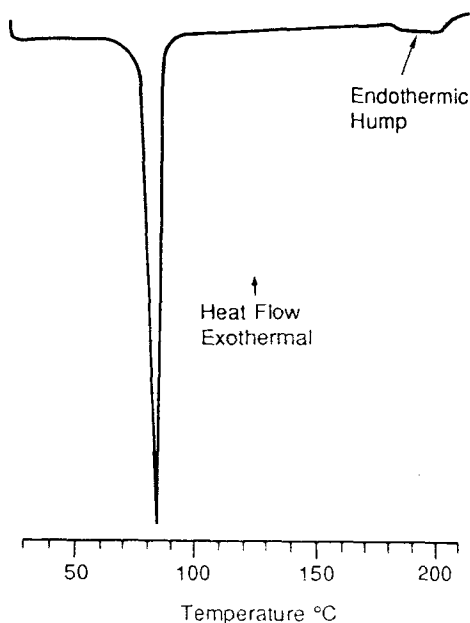


Fig. 5 Exothermic deviation above 190°C during heating cycle for TNT samples containing 7% HNS previously cycled from 20 to 225°C and reheated at 5 deg·min<sup>-1</sup>

mic peak between 200 and 180°C. This could correspond to a decomposition reaction. Several DSC samples were discoloured, ranging in colour from yellow to dark brown, after repeated thermal cycling above 175°C. Infrared spectra of these samples were identical with spectra obtained from the pure chemicals and the unheated mixtures. No additional materials were detected by HPLC on samples which had been heat cycled a number of times. Similar results were obtained with both pure and doped samples with the doped samples appearing most discoloured. The colour could be due to a small amount of decomposition occurring with the more volatile components being lost and residual carbon retained in the lattice being responsible for the colour. Also the repeat cycle reproducibility of the effect suggests that no major chemical reaction is involved. Samples with more than 10% HNS showed a broad endothermic peak above 180°C prior to the exothermic deviation during the heating cycle (Fig. 6) and a corresponding exothermic peak during the cooling cycle (Fig. 7). Since similar deviations were not observed with the pure components it is possible that the liquid TNT is migrating into the HNS and promoting a reversible phase change within the solid HNS, perhaps to the orthorhombic form identified by other workers [19]. Further work should identify the solid HNS phases, present at these elevated temperatures.

DTA experiments confirmed that some weight loss was occurring at temperatures in excess of 180°C. Crystals of TNT were found growing in the cooler regions of the DTA cell compartment. HNS appeared to accelerate this loss and reduce the threshold temperature at which it was observed.



**Fig. 6** Unknown endotherm in the heating cycle of TNT and 15% HNS previously cycled from 20 to 225 to 25°C at 5 deg·min<sup>-1</sup>

Earlier studies on enriched nucleant showed a second endotherm during the first heating cycle, but in subsequent cycles only a single TNT melting endotherm was seen. Our results confirm these observations. The second endotherm is thus due to unusual behaviour of TNT in the nucleant. Figure 8 shows the DSC curves obtained with the crude hot filtered sample of nucleant (a) and with the same material after the first vacuum sublimation purification (b). Further vacuum sublimation treatment, improved the nucleant purity to 96%, based on the relative areas of the two endotherms. A third refinement produced no TNT endotherm on the first heating cycle to 130°C but only the familiar nucleant peak at 115°C. The second heating cycle produced only the normal TNT endotherm at 80°C. Further examination of the nucleant endotherm (Fig. 9) showed that its shape is unlike the curves observed for the decomposition of a genuine charge transfer complex. The endotherm extends over a 20°C range and there is evidence of the presence of more than one endotherm indicating possible variation in structure and composition or a mixture of different materials. Similar endotherms are observed for solid solutions or inclusion compound decomposition involving the migration of one component inside the lattice of the other [21]. The included material melts out of the host lattice above its normal melting temperature and below the host's melting point. The changing shape of the endotherm during purification suggests a variable com-

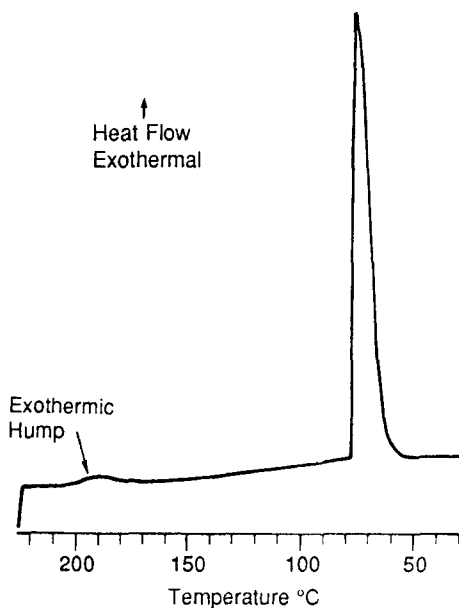


Fig. 7 Additional exotherm during cooling cycle for TNT and 7% HNS sample heated to 220°C at 5 deg·min<sup>-1</sup>

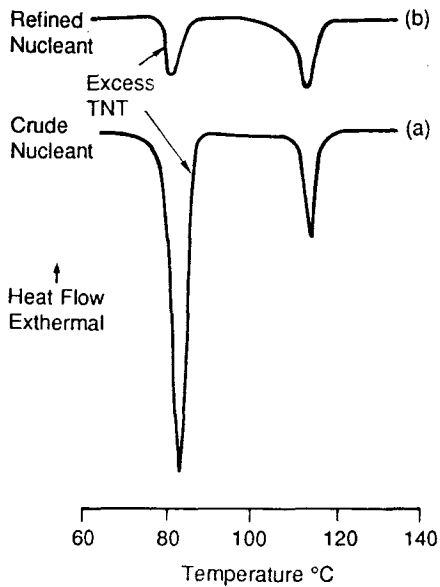


Fig. 8 DSC heating curves for (a) crude nucleant from filtration experiment; (b) nucleant from first vacuum sublimation experiment

position solid solution rather than a simple complex. Nucleant prepared by high temperature annealing may have a variable composition dependent on deposition temperature during cooling since the mobility of the TNT in the HNS and the solubility of HNS in the TNT are both temperature dependent. Further work on nucleant separated at different temperatures is required. Previous work with enriched nucleant observed the nucleant decomposition only during the first heating cycle and hence postulated a complex. This study has demonstrated a reproducible endotherm on subsequent heating cycles if, before cooling, the samples are heated to a sufficient temperature to redissolve the precipitated HNS into the TNT and cocrystallise the HNS with the TNT.

### *Nucleant composition*

The masses of TNT and HNS present in nucleant samples, were calculated from a comparison of the fusion enthalpies for excess and nucleant TNT with the pure TNT value. TNT endotherms before and after nucleant decomposition confirmed that fusion enthalpies for nucleant TNT and free TNT are equal. We assumed that HNS is only present in the nucleant form; the purification treatment removed only excess TNT and nucleant decomposition with loss of TNT was negligible. Data collected for the sample indicated in Fig. 8 were:

	TNT	Excess TNT	Nucleant	
			Original	Decomposed
Enthalpy /mJ	154	181	573	745
Mass /mg	1	1.17	3.71	4.82

Mass HNS = Sample mass - mass TNT = 11.11 - 4.82 = 6.29 mg  
 Mass TNT in nucleant = 3.71 mg  
 Ratio TNT:HNS = 37.1:62.9. Further samples of nucleant gave compositions ratios TNT:HNS of 36.3:63.7, 33.0:67.0, 34.6:65.4, yielding a mean nucleant molar composition TNT:HNS of 1.125:1. This ratio would only be consistent with the proposed complex nucleant composition 2:1, if purification removed 50% of nucleant TNT.

Formation of the nucleant is a balance between the solubility of HNS in TNT and the lattice strength of solid HNS. If the nucleant was a complex, the amount would increase linearly with concentration of the lowest component HNS up to the level of 50% by mass corresponding to the formula TNT<sub>2</sub>HNS. However, if the nucleant is a solid solution of TNT in HNS, then the quantity of nucleant formed will depend on the molar concentrations of both components. Nucleant concentration will pass through a maximum around the 5% HNS level due to the limited solubility of the HNS and the reduction in the amount of liquid TNT available to dissolve the HNS. Formation of a complex infers that the TNT HNS interaction, perhaps through hydrogen bonding, is stronger than either the TNT

TNT or the HNS HNS interactions. The low solubility of HNS in TNT does not support this hypothesis. If, however, the nucleant is a solid solution of TNT in HNS, then the free energy of formation would be derived from an entropy term associated with mixing a limited quantity of TNT in the HNS lattice. Free energy of mixing  $\Delta G_{\text{mix}}$  is given by the term [22]

$$\Delta G_{\text{mix}} = nRT\{x_a \ln x_a + x_b \ln x_b\}$$

where  $x_a$  and  $x_b$  are mole fractions of *a* and *b* respectively. The equilibrium would be a balance between an unfavourable lattice energy term and a favourable entropy term. In the liquid state the fluctuating HNS molecule could adapt to the TNT environment and produce supercooling for the 0.5% sample during the first cycle. Solid HNS exhibits a rigid chain conformation and cannot adapt to the TNT environment. Once solid HNS appears, further precipitation is favoured. If the temperature is not raised above that at which all the HNS dissolves, the nucleant would still be effective. Samples with HNS concentration above 1% heated to  $>110^\circ\text{C}$  showed no supercooling even during the first setting cycle.

**Table 2** Crystal unit cell parameters TNT and HNS

Compound	Space group	Unit cell dimensions /Å			
		a	b	c	$\beta$
TNT	P 2 <sub>1</sub> /c	21.23	6.08	14.958	110.12 °
HNS	P 2 <sub>1</sub> /c	14.693	5.585	22.159	108.44 °

Although the unit cell dimensions and space group of TNT and HNS are very similar (see Table 2), examination of the solid state structures indicates that the molecular stacking sequences are very different. There is space within the HNS lattice for a limited amount of TNT but the TNT lattice cannot accommodate the bulky HNS molecule resulting in poor miscibility of TNT with HNS. Further work on the mobility of TNT in the HNS lattice is required.

Spectroscopic evidence supports the formation of complexes between TNT and some aromatic nitrohydrocarbons or amines in which the TNT acts as an electron acceptor [23, 24]. These complexes are thermally unstable dissociating at temperatures below the melting point of both constituents. Complexes formed between 2,4 dinitrotoluene, *m.p.*  $71^\circ\text{C}$ , 1-nitronaphthalene, *m.p.*  $81^\circ\text{C}$ , and TNT decompose at  $47.5^\circ\text{C}$  and  $64.7^\circ\text{C}$  respectively. The proposed TNT HNS nucleant complex decomposes at temperature above the TNT melting point. The low mutual solubility of TNT and HNS is contrary to the solubility behaviour of established charge transfer complexes i.e. 1,3,5-trinitrobenzene and TNT form a ~1:1 eutectic [25]. Extended aromatic delocalisation over the car-

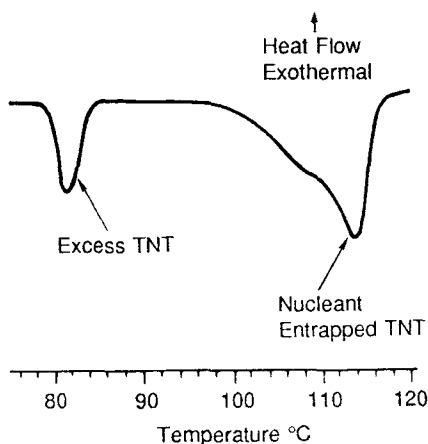


Fig. 9 DSC heating cycle for partially vacuum purified nucleant heated at  $5 \text{ deg}\cdot\text{min}^{-1}$

bon-carbon double bond linking the two aromatic rings in HNS reduces its donor capacity and provides extra stability for the HNS solid namely its high melting point. Reduction of the double bond to yield hexanitrobibenzyl reduces the nucleating properties and increases mutual solubility [17].

Nucleant could not be recrystallised from solvents. Only pure TNT or HNS or simple mixtures of TNT and HNS separated from solution. Therefore, even under the most favourable conditions, TNT and HNS preferred their own company to that of the other.

## Conclusions

DSC studies indicate that the effective nucleant which contains TNT and HNS is only formed by HNS which has been recrystallised from molten TNT and is a solid solution of TNT trapped in the HNS lattice. The variable composition of the nucleant indicates a solid solution rather than a charge transfer complex. Nucleant is thermally dissociated but can be reformed on cooling providing the concentration of HNS is in the range  $>1\%$  &  $<7\%$  of the TNT. Absence of sufficient TNT to dissolve all the HNS results in a decrease in nucleant quality and a poor munition filling. Nucleant cannot be recrystallised from solvents even in the presence of large excesses of TNT.

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**Zusammenfassung** — Zur Verbesserung des Gefüges wurde zu Trinitrotoluol (TNT) Hexanitrostilben (HNS) zugemischt. Unter Verwendung von Gemischen aus HNS und TNT im Bereich von 0.5- 50 Gew. % (HNS/TNT) wurde die Bildung und Zusammensetzung des keimbildenden Materiales mittels thermischen Methoden untersucht. Dies erfolgte cyclisch zwischen Raumtemperatur und einer oberen Temperatur im Intervall zwischen 160 und 235°C. Ohne erforderliche Trennung und Reinigung konnten in situ, infolge der Zersetzung des Keimbildners Endothermen im DSC-Verlauf beobachtet werden. DSC Enthalpiemessungen vor und nach der thermischen Zersetzung wurden zur Bestimmung der Zusammensetzung des separierten Keimbildners verwendet. Die Keimbildnerregenerierung nach der Zersetzung wurde mittels thermischer Methoden untersucht. Der Keimbildner konnte aus Lösungsmitteln nicht umkristallisiert werden. Die Ergebnisse wurden auf der Grundlage der Bildung einer festen Lösung von TNT in HNS und nicht eines Komplexes der Formel TNT<sub>2</sub>HNS interpretiert.