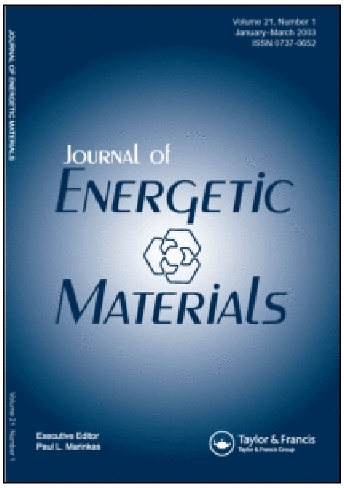

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Structural investigation of the crystallisation nucleant formed between 2,4,6 trinitrotoluene, TNT and 2,2',4,4',6,6' hexanitrostilbene, HNS

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STRUCTURAL 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

HNS nucleant, effective for TNT crystallisation & prepared from 3% HNS mixtures in molten TNT heated to 160 °C, has been examined by spectroscopic and x-ray diffraction methods. Solution UV/Visible spectra of pure nucleant were identical with mixtures of TNT and HNS. Powder x-ray diffraction patterns of the product differed from those of TNT and HNS and corresponded to unit cell parameters :- a = 10.685 Å, b = 5.684 Å, c = 14.421 Å, ß = 104.18°, V = 849.17 $Å^3$, Z = 2. The 'a' unit cell dimension is half that of normal HNS and the ß angle is reduced giving 2 molecules per cell. This pattern can be interpreted on the basis of a solid solution of TNT in HNS. The additional TNT in the HNS structure may remove the difference between the 'A' and 'B' type HNS molecules or modify the stacking sequence of the HNS molecules.

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INTRODUCTION

Extensive use of TNT in munitions, either as a high explosive composition or as an energetic binder for other high explosive compounds [1,2], is in spite of an ~11 % volume contraction [3] and extensive supercooling. The 15-20 °C reduction in the normal setting temperature 80.7 °C results in the production of highly oriented, needle shaped crystals, with their long axis normal to the sides of the shell casing [4]. The needle dimensions depend on the degree of supercooling, which controls their rate of growth. Anisotropic linear thermal expansion coefficients [5] cause the needles to separate during thermal cycling, increasing internal stress within the needles and producing undesirable voids between the needles [6]. Some TNT castings experience irreversible expansion during thermal cycling [6]. The shrinkage, on setting, can be overcome by using molten TNT headers above the munition during filling [7]. Vigorous stirring as the melt cools, producing a creamed material, or seeding the melt with finely ground TNT crystals, gently stirred in immediately prior to setting, reduces supercooling [8,9] and improves the randomness of the filling. Both of these techniques require careful operator control of stirring speed, temperature and rate of cooling.

Addition of small amounts, 0.3 to 0.5%, of HNS, an almost insoluble material, followed by a double thermal cycle [10], eliminates supercooling, produces more nucleating sites and promotes a smaller randomly orientated grain structure in the solid, with an improvement in the mechanical properties of the fillings. Repeated heating, above the molten state to 85 ^{0}C, does not remove the fine grain texture of the cast solid when cold. Above 90 ^{0}C the nucleant is destroyed but can be regained by heating to > 115 ^{0}C and repeating the Bofors cycle. Pure, separated, nucleant decomposes above 85 ^{0}C and is not reformed by further heating cycles regardless of temperature [11,12]. During nucleant decomposition TNT appears as a melt on the surface of the solid. A complex, of formula TNT_2HNS, which was not observed during the first heating cycle, but appeared to form as the TNT began to melt during the reheat cycle, has been proposed as the effective nucleant. The nucleant appeared to be a separate crystal from both TNT and HNS. A limited, inaccurate x-ray diffraction pattern from separated nucleant [13], showed a different pattern from those of TNT or HNS, but was insufficient to establish the true nucleant identity. The variable composition of the nucleant [14] suggests that a simple, unique composition complex was not the active material.

TNT exists in two primary crystal structures, monoclinic and orthorhombic [15,16]. Both crystal forms can be obtained by crystallisation from solvents or the molten phase under controlled conditions. When heated, the orthorhombic structure is reported to change into monoclinic form at or just before the melting point [17]. A number of variations on the TNT structure arise from formation of twinned fragments of the monoclinic and orthorhombic forms, aligned with respect to their pseudo-orthorhombic axes, which are best represented by the basic unit cells or by simple polytpic multiples of the b unit cell dimensions [18]. These polytypes are readily formed during the melting process and produce mixed melting temperatures with associated microscopic activity. Also these polytypes exhibit variable intensities for the x-ray powder reflections associated with the superlattice structure. HNS crystalises in a monoclinic form and a comparison of the unit cell dimensions of the monoclinic forms of TNT and HNS are given in the table below [19,20].

TABLE 1

Crystallographic properties of Monoclinic TNT & HNS

	Unit Cell Dimensions Å				Space	Atoms in
Compound	'a'	'b'	'c'	ß(°)	Group	Unit Cell
TNT	21.23	6.08	14.958	110.12	$P2_1/c$	8
HNS	22.159	5.585	14.693	110.04	$P2_1/c$	4

Although TNT and HNS have similar molecular and crystal structures the low solubility of HNS in TNT (0.3% at 81

°C) indicates that the lattice energy of the HNS is greater than that of mixed materials. Hexanitrobibenzyl, HNBB, although similar in many ways to TNT and HNS, is readily soluble in TNT, but is a poor nucleant for TNT. This study examines some properties of solids deposited from solutions of HNS, in solvents and in molten TNT.

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., Poole, Dorset. Details of the purification processes and analysis have been described elsewhere [21,22]. Purified TNT and HNS were found to be >99.9 % pure with no evidence of HNBB the normal impurity in HNS.

Nucleant Preparation and Purification

Raw nucleant was prepared either by standard Bofors cycle or by melting 3% HNS / TNT mixtures at 160 °C, and filtration at 85 °C. Details of the methods have been described elsewhere [23]. Filtered nucleant was separated from the TNT contamination, indicated in figure 1, by modified literature methods using vacuum sublimation at 75 °C and 10^{-2} mm Hg for 48 hours [24,25] until the DSC trace showed no evidence of the free TNT melting endotherm. Increased solubility of HNS in TNT at higher temperatures, around 170 ^{o}C, should increase the yield of the effective nucleant and also provide information on the phase diagram for the mixture. Recrystallisation of nucleant from a range of different solvents saturated at different temperatures from boiling temperatures to 20 ^{o}C was also examined.

Thermal Analysis

DSC experiments were performed on 10-30 mg samples of the separated nucleant, using a Mettler TA 4000 system fitted with a DSC 30 chamber and TC 11 TA Processor, to check its purity and composition, from the relative areas of the free TNT and nucleant endotherms before and after decomposition.

Spectroscopy Measurements

Samples of TNT, HNS and nucleant, were prepared for solid state UV/Visible spectroscopy by rubbing a standard Whatman filter paper in the solid until an area, greater than the beam dimensions, 2 by 0.3 cm, was impregnated with the solid. The filter paper was then mounted in the reflectance attachment of a Perkin Elmer " Lambda 9 " spectrometer and spectra recorded over the range 2000 to 185 nm.

Solution UV/Visible spectra of TNT, HNS and nucleant in chloroform, acetone, acetonitrile, N-methyl pyrolid-2-

one and cyclohexane were recorded using silica 1 cm path length cells on a Perkin Elmer "Lambda 2 " spectrometer. Infra-red spectra of TNT, HNS and nucleant were recorded using "Nujol" mulls on a Mattson " Polaris" model spectrometer.

X-Ray Measurements

Finely ground solid samples were sprinkled onto a thin smear of silicone grease, on a silica slide mount on the sample stage of a Siemens D 500 powder diffractometer in the Bragg Brentano focussing condition. X-ray diffraction data was collected over the Bragg angles (2θ) from 16 to 55^0, using Copper K_a radiation with a graphite monochromator in the detector beam, under the control of an IBM " AT " compatible computer, operating the ISIP suite of software [26]. Data analysis was performed using the indexing program " POWD " [27] and Reitveld analysis was performed using the " Reitan " program [28]

RESULTS AND DISCUSSION

Thermal Studies

DSC studies confirmed our earlier conclusion that the nucleant could be produced by repeated heat cycling of TNT samples containing HNS in the range >1% <7% above the nucleant decomposition temperature and, by the absence of the appropriate endotherm, that nucleant could not be recrystallised from solution [19] even at room temperatures. Also purified nucleant composition was determined as a mole ratio of TNT to HNS of 1.13:1 ±0.02. Although all the HNS was soluble in the molten TNT at the temperatures and compositions used, it is possible that some pure HNS is precipitated with the nucleant, when the solution is cooled to 85 ^{o}C. Nucleant which was produced by filtration at 85 ^{o}C after setting and remelting gave identical DSC thermograms. Further experiments with material, initially precipitated from solution, after cooling from 170 ^{o}C to 130 ^{o}C and isolated at that temperature, are planned. TNT losses from nucleant, during purification , would have to be high to produce the previously proposed complex nucleant composition of 2:1. Further experiments on the effect of conditions during nucleant purification on the nucleant compositions are also planned.

Spectroscopy

UV/visible spectroscopy of solid samples of HNS, TNT and nucleant indicated that removal of the excess TNT from the nucleant surface changed the spectrum from being similar to that of TNT to that resembling the HNS, without demonstrating any features unique to the nucleant, (figure 2). Nucleant solution spectra, in all the solvents, were simple additions of the TNT and HNS spectra, (figure 3). Nucleant solutions changed colour during preparation, but this was due to the differing dissolution rates for TNT and HNS from the nucleant.

Peak position shifts and the presence of additional absorption bands in the UV/Vis spectrum are indicative of complex formation between TNT and aromatic amines or nitrohydrocarbons, in which the TNT acts as an electron acceptor [29,30]. These complexes are thermally unstable and dissociate at temperatures below the melting point of both constituents. Complexes formed between TNT and 2,4 dinitrotoluene, M.Pt 71 °C, and 1-nitronaphthalene, M.Pt. 81 °C, decompose at 47.5 °C and 64.7 °C respectively. The TNT / HNS nucleant decomposes above the TNT melting temperature. Complex formation normally depends on the lowest component concentration and for the formula TNT_2HNS, the amount would be expected to increase almost linearly with HNS concentration, up to the critical level of 50% by mass. If the nucleant is a solid solution of TNT in HNS, whose formation is energetically unfavourable then it's concentration will depend on the molar concentrations of both components and will reach a maximum around the solubility limit of HNS in TNT (< 1%.) at 80 °C and ~4% at 180 °C. 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 where a ~1:1 eutectic composition is formed [31]. Further work on the mobility of TNT in the

HNS lattice, during purification conditions, is planned since some thermal studies [20] exhibit endotherms characteristic of diffusion processes.

Infra-red spectroscopy on the nucleant indicated no additional bands simply a supposition of the TNT and HNS spectra. It is unlikely that simple adjustments in the orientation of the nitro groups would have a significant effect on any of the vibrational mode energies of either the nitro groups or the aromatic skeleton and hence there will be no change in the observed spectrum.

X-Ray Diffraction

A mixed sample of the two crystallographic forms of TNT, produced by incomplete recrystallisation from cyclohexanol, gave the diffraction pattern shown in figure 4a. The HNS pattern, figure 4b, corresponded to the literature monoclinic unit cell[19], with a figure of merit [32] at line 30 of 15.7. TNT with added HNS always recrystallised in the monoclinic form even when quenched [21]. Solids produced from the mixed TNT and HNS solutions in solvents gave X-ray powder diffraction patterns which corresponded to TNT, or HNS, or simple mixtures of the two.

Once the surface excess TNT has been removed, the nucleant x-ray powder pattern does not clearly identify with either of the pure components. Figure 5 shows an expanded low angle region. The position and intensity of a number of the HNS reflections appears to have changed but there is no sign of the normal HNS pattern and hence the quantity of free, non-nucleant, HNS must be <5%, the limit of detection for this x-ray method. The lattice parameters and the cell contents, for the purified nucleant, determined from the indexing program, differ from those of the original HNS cell see table 2.

TABLE 2

Linear Least Squares Unit Cell Fit to X-Ray Powder Data
from Purified Nucleant Sample

```
Sys.MONO. S.G.P1*1  Lambda= 1.541780 F25= 17.0(0.007,203)
a=14.4210A. b= 5.6840 c=10.6850 beta=104.180D. V=  849.15
 d-spacing A.    Indices  SinSqTheta*E4   2Theta Deg.
obs.   calc.     h  k  l  obs.   calc.    obs.   calc.
----------------------------------------------------------
5.2646  5.2655   1  1  0  214.4  214.3    16.84  16.84
5.1791  5.1797   0  0  2  221.6  221.5    17.12  17.12
4.9828  4.9832   0  1  1  239.4  239.3    17.80  17.80
4.5255  4.5283   1  1  1  290.2  289.8    19.62  19.60
4.4022  4.4102   2  1  0  306.7  305.5    20.17  20.13
3.9829  3.9836  -3  0  2  374.6  374.5    22.32  22.32
3.8273  3.8285   0  1  2  405.7  405.4    23.24  23.23
3.7447  3.7460   2  0  2  423.8  423.5    23.76  23.75
3.5617  3.5617  -1  0  3  468.5  468.5    25.00  25.00
3.4504  3.4497  -2  0  3  499.2  499.4    25.82  25.83
3.2218  3.2198   3  1  1  572.5  573.2    27.69  27.70
3.0914  3.0905   4  0  1  621.8  622.2    28.88  28.89
2.9516  2.9512   0  1  3  682.1  682.3    30.28  30.28
2.7866  2.7850   1  2  0  765.3  766.2    32.12  32.14
2.7152  2.7151   4  1  1  806.1  806.1    32.99  32.99
2.6516  2.6491  -2  0  4  845.2  846.8    33.80  33.84
2.4973  2.4973   3  0  3  952.9  952.9    35.96  35.96
2.4410  2.4417   1  0  4  997.4  996.8    36.82  36.81
2.4013  2.4012  -2  1  4 1030.6 1030.7    37.45  37.45
2.3135  2.3136  -3  2  2 1110.3 1110.2    38.93  38.93
2.2282  2.2280  -4  2  1 1197.0 1197.1    40.48  40.49
2.1523  2.1523  -4  2  2 1282.9 1282.8    41.98  41.98
1.8730  1.8730   4  0  4 1694.0 1694.0    48.61  48.61
1.8369  1.8368   1  3  1 1761.2 1761.3    49.63  49.63
1.7574  1.7574  -3  3  1 1924.2 1924.1    52.04  52.04
```

The indexing program had to be modified to accommodate the low intensity reflections above $2\Theta = 35^0$ because the refinement routine applied zero weight to these weak reflections. In the original format calculation of the unit cell dimensions was based on only 14 indexed lines with a figure of merit, F14, of 27. Incorporation of the higher angle lines reduced the figure of merit F25 to 17 and produced a minor change < 0.01% in unit cell volume.

Crystal structures for both the two forms of TNT and HNS contain equal number of two types of molecules, A and B, which differ in the torsion angles of the nitro groups in the 2,4 and 6 positions, with respect to the aromatic ring [33]. Incorporation of TNT into the HNS lattice could restrict the torsion angles of the nitro groups, removing the difference between type A and B molecules in the original HNS structure, thus reducing the unit cell dimensions and contents. It may well be possible that there is a range of compositions for the nucleant which will have the same basic structure but with the unit cell dimensions depending on the exact composition as found for solid solutions [34,35]. Further work on this aspect will be required

Examination of the solid state structures for HNS and TNT, figure 6, indicates that, even though the space groups are identical and the unit cell dimensions are very similar, the molecular stacking sequences in the TNT and HNS structures are very different. Projections of the unit cell contents onto the ac plane for both materials, shows a correspondence between two molecules of TNT and one molecule of HNS, but the projection does not indicate the difference in height, in the b direction, of the aromatic planes of HNS occurring at the ethylenic linkage joining them. The aromatic rings are closer together in HNS than in TNT and hence this would suggest that, epitaxy of TNT on the 010 plane of HNS is unlikely. Projection of the two structures on the 001 plane shows the similar herringbone molecular pattern in the two structures, but whereas the TNT aromatic ring is parallel with the c axis, in HNS the aromatic rings make an angle of 45^{o} with this axis. Also the HNS molecules are not flat within the ab plane (figure 7). The similar stacking pattern means that epitaxy of TNT on the -1,0,1 plane of the HNS is possible. However epitaxy of TNT readily occurs with the optimum nucleant, HNS containing some TNT in its structure and recrystallised from excess of molten TNT. Since the nucleant powder data did not fit any of the known HNS structures a new form has been produced, which will require a full structure determination. Experiments are under way to prepare suitable single crystals.

There may be limited space, within the HNS lattice, near grain boundaries or other imperfections, for a very limited quantity of TNT to be incorporated during crystallisation. It is also possible that the TNT forms a "clathrate" in the HNS lattice expanding the lattice planes and reducing some of the x-ray reflections. This would result in an expansion of the cell dimensions in preferred directions. A more probable situation is that two TNT molecules could replace a single HNS molecule in the HNS lattice, with a consequent modification of the HNS lattice, in order to accommodate the additional four hydrogen atoms from the two TNT molecules. This local deformation of the lattice could then cause an extensive readjustment to extend over the remaining cells changing the structure observed with the x-ray pattern. TNT is only incorporated in the HNS lattice under conditions of excess TNT, which can interfere with the crystallisation process. Further work is required on this aspect. The TNT lattice cannot accommodate the bulky HNS molecule because of the different spatial geometry of one HNS molecule compared to two adjacent TNT molecules.

The lattice strength of solid HNS is greater than that of the mixed TNT HNS solid or pure TNT, resulting in poor solubility of HNS in TNT and the ready decomposition of the nucleant when the excess is removed. The melting point of HNS, 321 ^{o}C, is 200 ^{o}C above the nucleant decomposition temperature. Incorporation of TNT into the HNS lattice must be unfavourable since the nucleant is only formed under conditions of excess TNT, when an entropy of mixing G_{mix}, estimated to be about 3 kJ mole^{-1} for 3% TNT in HNS can stabilise the nucleant [36]. Nucleant becomes thermally unstable when the excess TNT is removed. Once solid HNS nuclei appear in the melt, further precipitation of HNS is favoured. If the melt temperature is not raised above that required to decompose the nucleant and dissolve the HNS, the nucleant once formed would still be effective. Samples with HNS concentration above 1% heated to >110 °C showed no supercooling even during the first setting cycle.

Solid HNS exhibits a rigid chair conformation about the double bond and can not adapt to the TNT environment , but in the liquid state the fluctional HNS molecule could adapt to the TNT environment and produce supercooling for the 0.5% HNS samples during the first cycle thus requiring the double thermal cycle.

Attempts to fit the x-ray data to a simple molecular structure by the Reitveld method proved unsuccessful probably due to the limited range of data available, or the absence of a genuine molecular structure. A solid solution of TNT in the HNS lattice would not require a definite arrangement of the included TNT.

Although the carbon carbon double bond, linking the two aromatic rings in HNS, might be expected to be a good electron donor, the extended aromatic delocalisation over this bond reduces it's donor capacity and provides extra stability for the HNS solid as revealed by the high melting point. When the double bond is reduced to form a related compound, HNBB, the nucleating properties are decreased and the mutual solubility increased [10].

Nucleant could not be recrystallised from any of the solvents tried. Only pure TNT or HNS or simple mixtures of TNT and HNS separated from solution. This indicated that, even under the most favourable conditions, with poor donor hydrocarbon solvents, TNT and HNS preferred their own company to that of the other.

CONCLUSIONS

Nucleant was unstable in solution and could only be prepared under conditions of excess molten TNT. X-ray powder diffraction pattern of the nucleant was different from those of TNT and HNS arising from a Unit cell of dimensions a = 10.6848, b = 5.6843, c = 14.4211 Å, ß = 104.18 °, V= 849.17 $Å^3$ and contents Z = 2. Reduced cell contents indicates either removal of the distinction between 'A' and 'B' type molecules found in normal HNS and TNT or a difference in the lattice stacking sequence in the HNS structure.

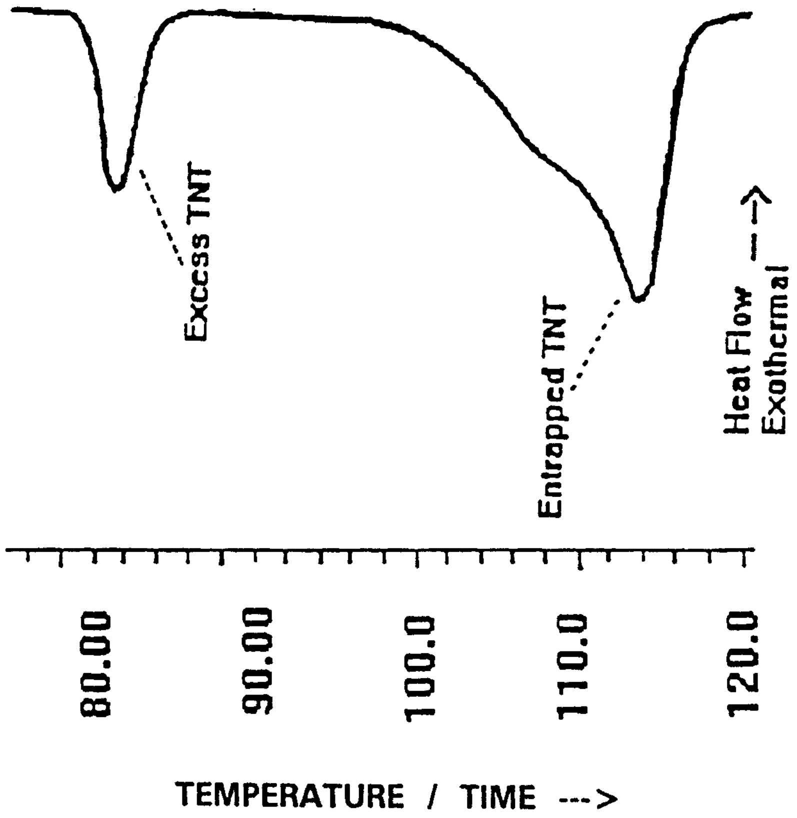

Figure 1
DSC traces from sample of filtered nucleant showing endotherms for excess TNT and nucleant TNT

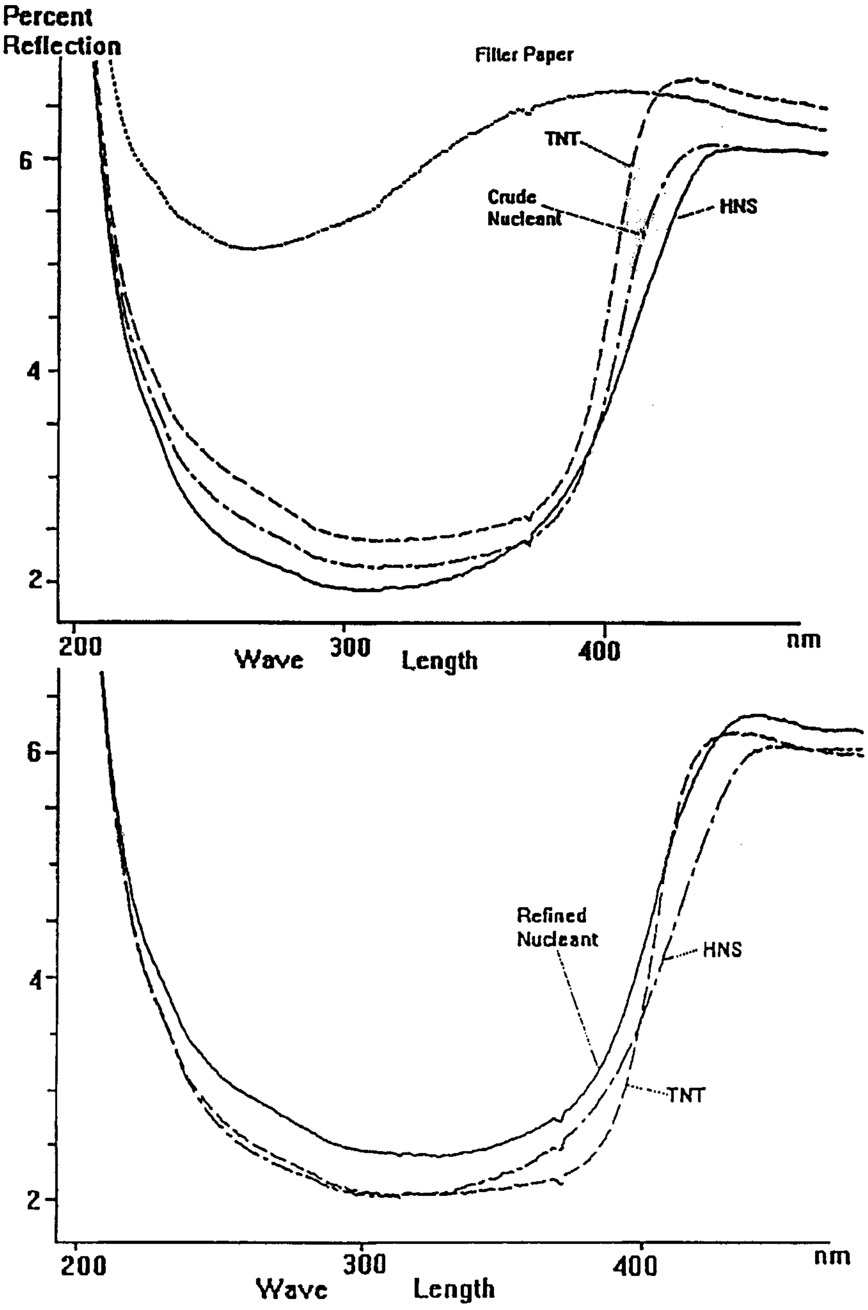

Figure 2
Comparison of UV/Visible reflectance spectra from solid nucleant during purification with those of TNT and HNS

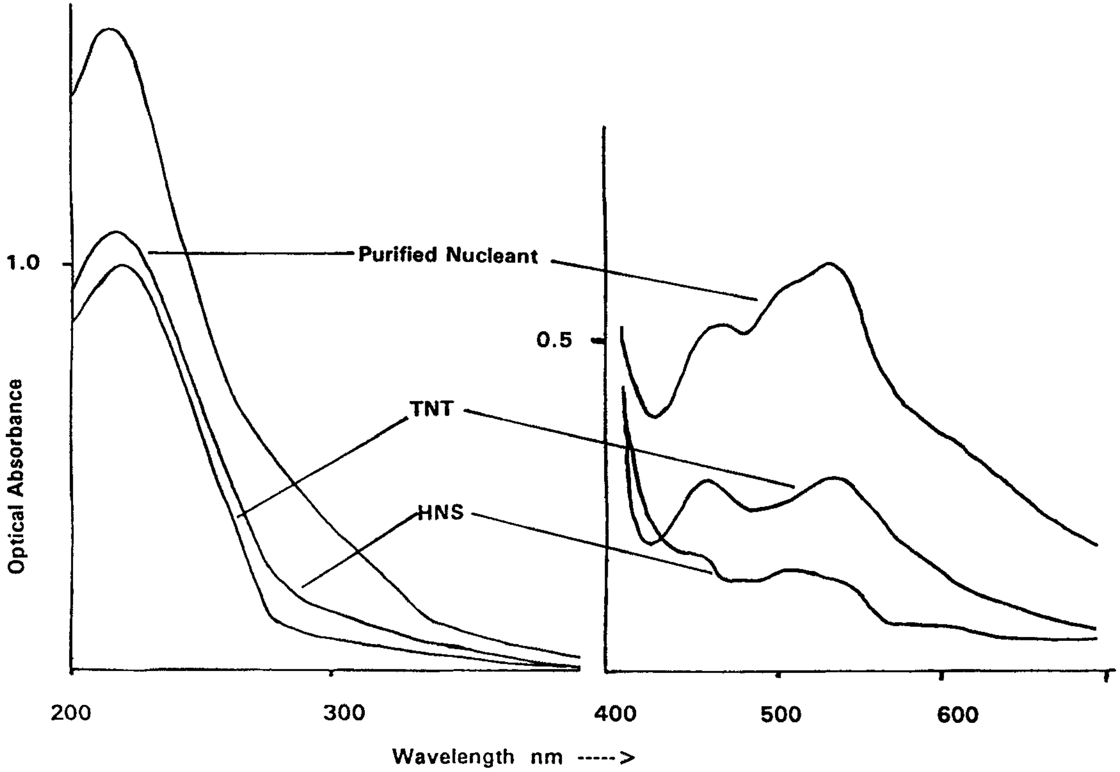

Figure 3
Solution UV/Visible spectra from TNT HNS and purified nucleant (a) ~ 10^{-3} M and (b) ~ 10^{-1} M solutions

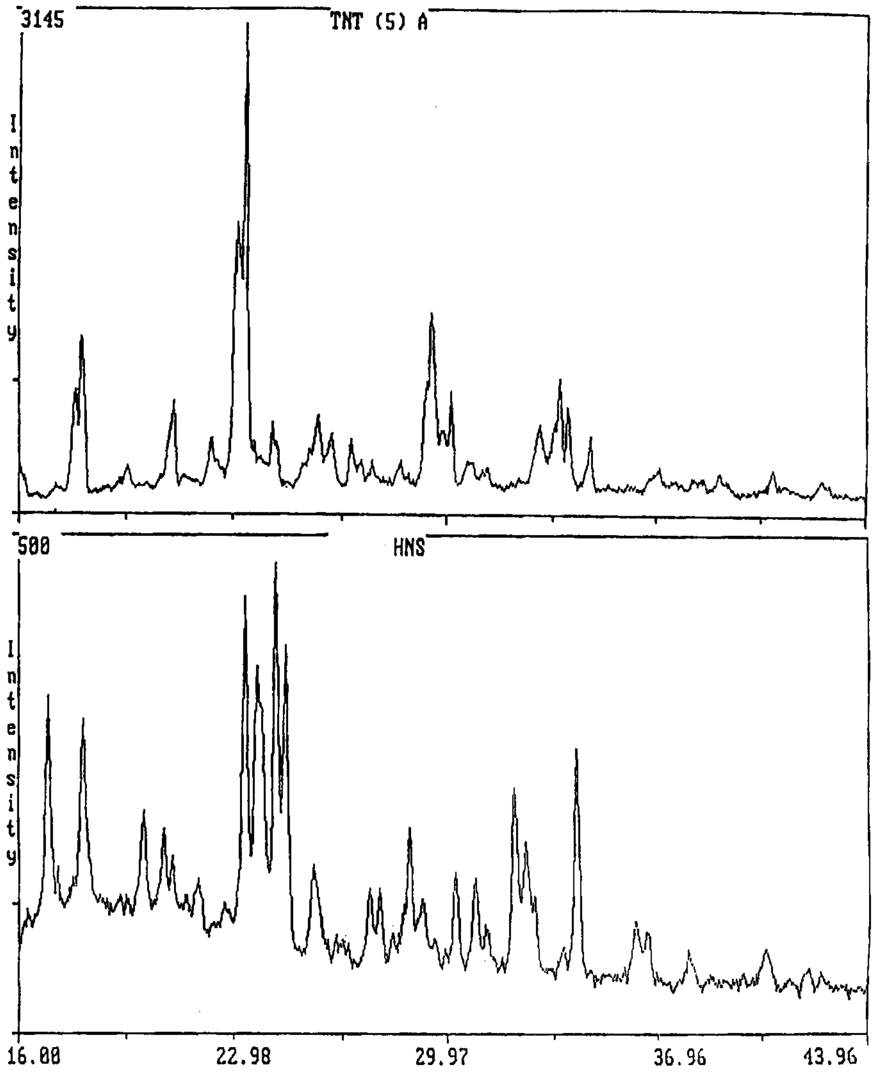

Figure 4
X-ray Powder diffraction patterns from a mixture of the two crystal forms of TNT (a) and HNS (b)

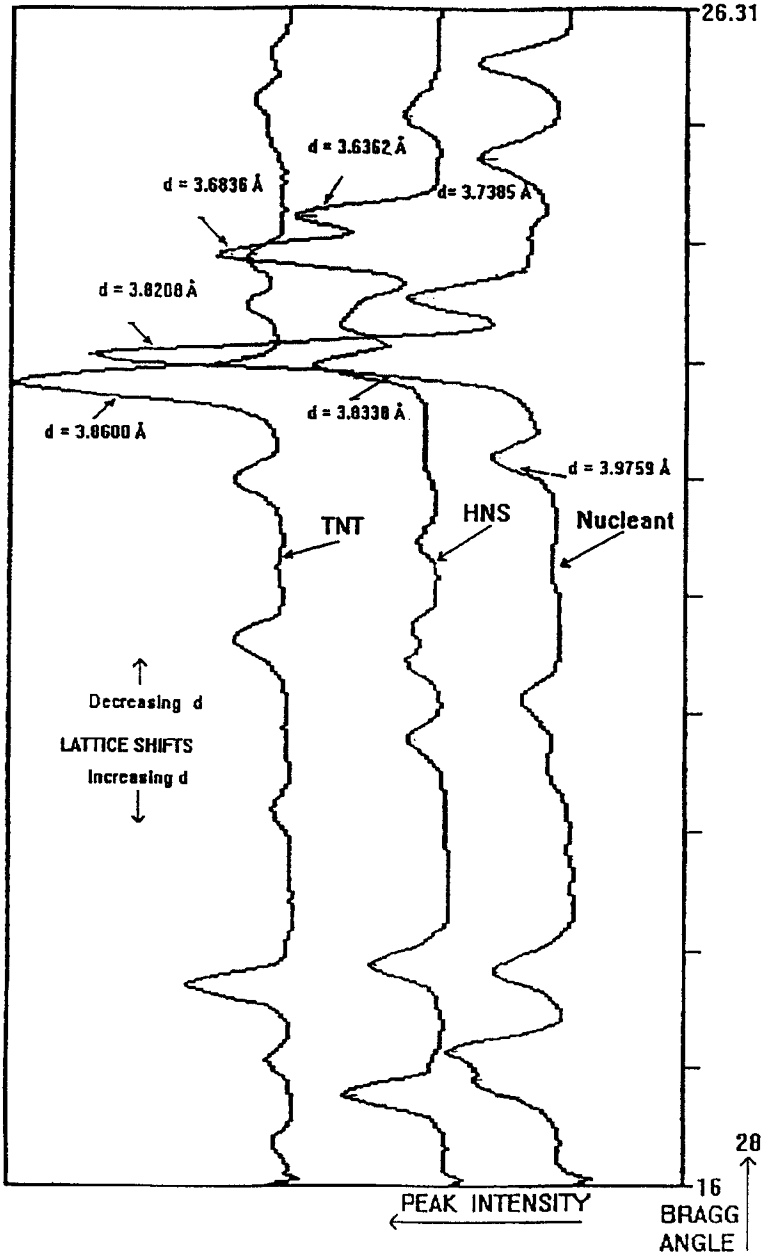

Figure 5
Comparison of the X-ray powder pattern from pure nucleant with those of TNT and HNS in the range 16-25° (2θ)

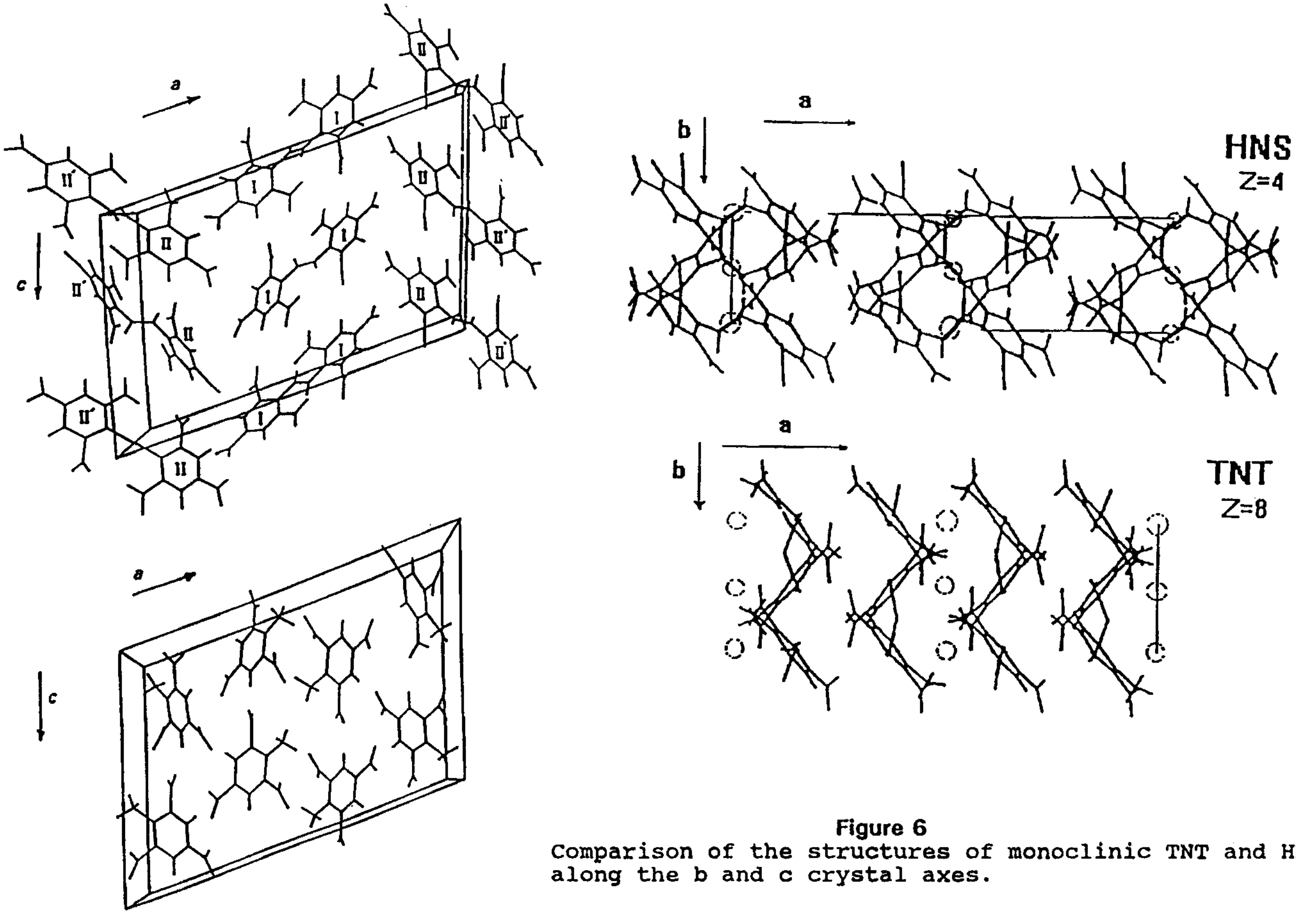

Figure 6
Comparison of the structures of monoclinic TNT and HNS along the b and c crystal axes.

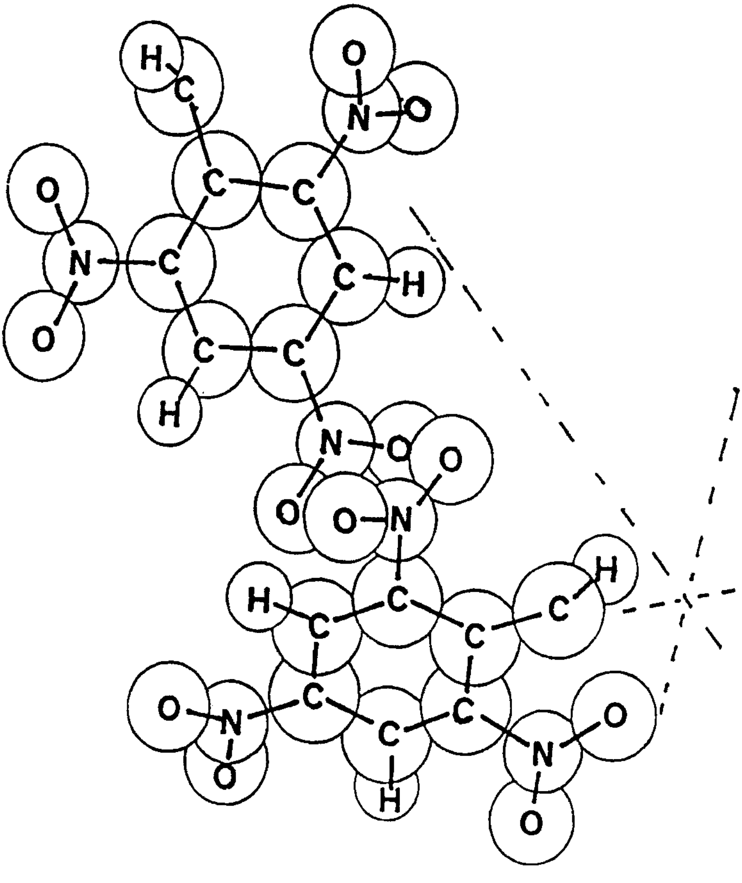

Figure 7
Two assymetric units of adjacent A and B molcules of HNS showing by the extent of the obscuration the non parallel aromatic rings and twisting of the nitro groups.

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