Research Article

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Microhardness Indentation Studies of 2-4-6 Trinitrotoluene

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Abstract: The microhardness of the {001} faces of 2-4-6 trinitrotoluene crystals has been investigated using both Vickers and Knoop indentation methods. The Vickers hardness number was found to be 22.5 kg mm^{-2} independent of crystal orientation and perfection. At ambient temperatures (~20 °C) the Knoop hardness number varied between 20.5 kg mm^{-2} and 24.0 kg mm^{-2} with crystal orientation. At higher temperature (50 °C) the Knoop hardness anisotropy curve retained its shape, although the overall hardness decreased by 10%. We interpret this change as reflecting a simple temperature dependant loosening of the crystal lattice rather than any change in deformation mechanism. No variation of Knoop hardness was evident with changing load. The hard direction was [010] and the soft [100]. The dominant operative slip system was defined to be {001}[010].

Keywords: TNT · Microhardness · Mechanical properties

1 Introduction

The understanding of the behaviour of organic materials is defined by not only their crystal structure, but also their defect structure, which governs many of their mechanical properties. Defect structure can be studied by technologically simple and complex means, e.g. from etching through to x-ray topographic studies. However, to understand better the mechanical properties, it is important to describe the interrelationship between defects and their host structure.

In particular mechanical deformation by indentation is a relatively simple technique that can be extremely useful in defining the mechanical properties that any given material may exhibit. With the wide expansion of interest in fine chemicals and especially the processing of pharmaceutically active compounds, the understanding of these structure property relationships has become ever more important. [1,2]. However, although such studies are commonplace for metals [3,4], they are less so for organic systems. Microindentation has been used in the examination of semi-organic non-linear optical materials [5–8], foodstuffs [9], pharmaceuticals [10,11] and energetic materials [12–17]. In addition to this, other mechanical methods have also been of use, such as frictional testing of energetic materials [18] and sorting of organic polymorphs through mechanical means [19]. Nanoindentation is a relatively modern technique which has been applied successfully to a range of energetic materials, e.g. for RDX and HMX [20–24]. The method is confined to the very smallest scales and generally yields higher values of hardness for a given material. Microhardness methods are complementary but sample larger volumes. Therefore, they yield information at a significantly larger size scale and provide orientational control which is more difficult to achieve using the nano-method.

In this study, we examine the microhardness properties of 2-4-6 Trinitrotoluene (TNT), a well-established secondary explosive. TNT is a relatively common energetic material although to some extent it has been superseded as an energetic material by others such as cyclotrimethylenetrinitramine (RDX), it still has a use due to its ability to be melt cast and is yet to be broadly replaced by less sensitive materials such as 2–4 dinitroanisole (DNAN). Thus, its applicability and relative stability with respect to detonation means that it is still of use in the modern world. In addition to its external applications, TNT is itself of intrinsic interest to structural chemists, due to its remarkable polymorphic properties. TNT has been a long-studied material and as with many organic materials, it has been shown to be polymorphic in nature [25]. Two possible unit cells are known to exist, monoclinic and orthorhombic. The monoclinic form is the most (thermodynamically) stable and has a unit cell of $a = 1.4911$ nm, $b = 0.6034$ nm, $c = 2.0882$ nm, $\beta = 110.36°$, (at $T = 150$ K) space group $P2_1/a$. The asymmetric unit of the monoclinic form contains two molecules of TNT, which have slightly different molecular conformations. The relationship between the two polymorphs is now well understood [26], with the differences being induced by effective stacking faults causing the different polymorphs. In addition to this a thorough examination of the

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growth processes and distribution of dislocations has also been made [27, 28], as has a theoretical study of the relative stability of the two forms [29]. This study is based upon the stable monoclinic form and completes a detailed and comprehensive study of the solid-state properties of monoclinic TNT.

In addition to the general understanding of organic molecules, hardness testing is important in the understanding of the behaviour of energetic materials [30–34]. It has been shown to be feasible that dislocation pile-up can cause localised "hot-spots" and can lead to premature detonation [35, 36]. Such information has led to a wide study of a number of commonly occurring energetic materials, such as Pentaerythritol Tetranitrate (PETN), Cyclotrimethylenetrinitramine (RDX) [1, 12, 14, 16, 37] and β-Cyclotetramethylenetetranitramine (β-HMX) [13, 17, 38], with both RDX and HMX also studied at the micro- and nano-indentation scale. These two scales are complementary, the latter having the advantage of smaller crystals and thus safer working, the former giving a broader orientational understanding of the properties. Although insults due to impact have been shown to be sub-critical in nature [34], this is not yet known for other forms of insult, e.g. cook-off. Indeed, the recent computational work by the Morrison group [39, 40] has shown a possible way forward in understanding how impact sensitivity is affected by crystal structure, and thus it leads to the concept that defect structure, mechanical properties and deformation are still an important part of understanding sensitiveness in energetic materials.

2 Experimental Section

Materials Purification and Crystal Growth: TNT was supplied by PERME, Waltham Abbey, as standard military grade. The source material was purified using the sodium sulphite method [41] which removes unsymmetrical trinitrotoluene isomers, dinitrotoluenes and other derivative based impurities. Chromatographic analysis showed that the resultant material was $>99.9\%$ pure.

Crystals of monoclinic TNT were grown at room temperature (293 K) by the slow evaporation of saturated solutions in ethyl acetate, (Sigma-Aldrich standard grade purity 99% +). As can be seen from Figure 1 these show the typical coffin shaped morphology and the large (001) faces associated with monoclinic TNT.

The perfection of the samples, which could be influential in determining the microhardness, was assessed by dislocation etching. This was carried out using methanol (Sigma-Aldrich, purity 99+%) as solvent, the crystals being etched for periods of up to 1 second at 20 °C.

Microhardness measurements: These were carried out on the {001} habit faces using a Leitz Miniload microhardness tester, fitted with either Vickers or Knoop pyramidal indentation heads. For Vickers indentation, measurements were made as a function of crystal orientation and surface perfection at a load of 15 g. In the case of Knoop indentation, the measurements were made as a function of load (15–50 g), temperature (295 K and 323 K) and crystal orientation. All hardness values at room termperture represent the mean of values calculated for a minimum of at least 10 impressions at each experimental point, for higher temperatures, at least 6 measurements were taken for each point.

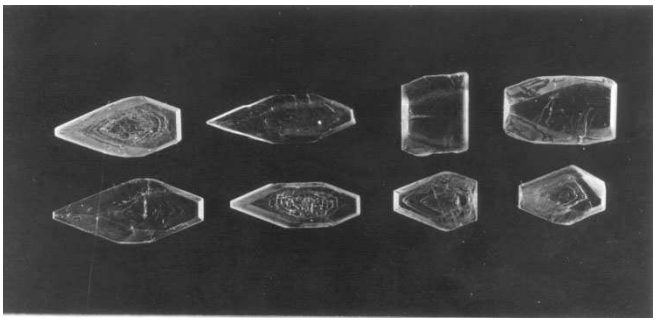

Figure 1. The typical habit of the monoclinic TNT crystals used in this study.

3 Results and Discussion

The effect of crystal orientation on Vickers microhardness was observed by indenting the crystal initially with the indenter diagonals parallel to [010] and [100] and then with the diagonals at an angle of 45° to these directions (Figure 2, larger images and an orientational diagram can be found in the electronic supplementary information S1). It can be seen that with the indenter diagonals lying parallel to [100] and [010] (Figure 2a), the indentation shape is slightly concave, cracks exist lying parallel to [010] and interference fringes surround the indentation. Optical microscopy shows that the cracks that lie parallel to [010] are inclined to the crystal surface and thus appear to lie in the

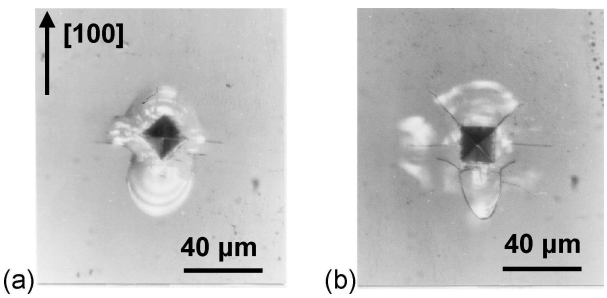

Figure 2. Vickers hardness impressions made using a 15 g load with a diagonal (a) parallel to and (b) at 45° to the [010] and [100] crystallographic directions.

{100} planes and the interference fringes are caused by partial cleavage on {001} planes.

Such cracking along [010] and interference fringes are also apparent when the indenter diagonal lies at an angle of 45° to [010] and [100] (Figure 2b). However in this case the indentation shape is convex and irregular cracks lie at 45° to [010]. These additional cracks do not correspond with any known crystallographic direction of TNT. The extent of fracture was invariably greater for indentation at 45° to [010] and [100] than for indentation at the other orientation. The VHN for indentations parallel to and at 45° to [010] and [100] were calculated to be 22.5 kg mm^{-2} and 22.4 kg mm^{-2} respectively at a temperature of 295 K.

Etching of the {001} faces of numerous small TNT crystals of the type used in the microindentation hardness studies revealed a consistently low number of relatively large, shallow etch pits (density $< 10^2$ cm^{-2}) distributed in a characteristic pattern across the middle of the crystal with only a few individual pits found at the extended ends, consistent with the defect structure observed in previous topographic studies of TNT [27]. The results showed no significant variation in hardness with the VHN lying in the range 22.3 to 22.6 kg mm^{-2} for the range of dislocation densities assessed.

The variation in Knoop hardness number (KHN) with indenter orientation at different loads between 15 g and 50 g, at a temperature of 295 K is given in Figure 3. The KHN was independent of load and varied with orientation in the range 20.5–24.0 kg mm^{-2}. The hard and soft directions were found to correspond to the [010] and [100] crystallographic directions. An example of several Knoop indentations made using various loads is shown in Figure 4 (Larger diagram in ESI S2). It is of note that nanoindentation values of 17.4 kg mm^{-2} and ~49 kg mm^{-2} have been reported by Wen et al. [42] and Zhu et al. [43, respectively]. Both these values differ significantly from the hardness values found here, possibly reflecting differences in the small volumes of material assessed.

It can be seen that the extent of cracking obtained with this type of indenter is considerably reduced in comparison with that developed by the Vickers indenter. No lateral cracks were observed but those parallel to the surface remained significant. The variation in KHN at a temperature of 295 K and 323 K with a 15 g load is illustrated in Figure 5. The two curves have the same shape with the overall hardness being 10% lower at the higher temperature. This implies that there is little change in the deformation characteristics with temperature.

The effective resolved shear stress (ERSS) model of Daniels and Dunn [3] and the later modification by Brookes et al. [4] have been used successfully to explain the anisotropy of Knoop hardness in many single crystal systems. Both these analyses consider the KHN as an inverse function of the ERSS developed on the slip system which accommodates dislocation motion during indentation.

Since there are no previous examinations of dislocation migration in TNT, it is necessary to speculate on potential slip systems on the basis of the crystal structure. The Peierls-Nabarro model [44] predicts that dislocation slip will

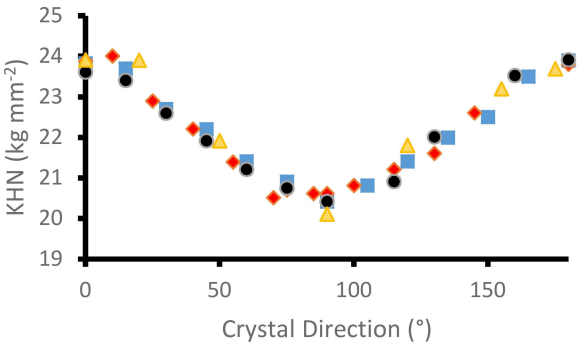

Figure 3. The variation in KHN with crystal orientation and load. 15 g (■); 25 g (◆); 35 g (●); 50 g (▲) at T = 295 K.

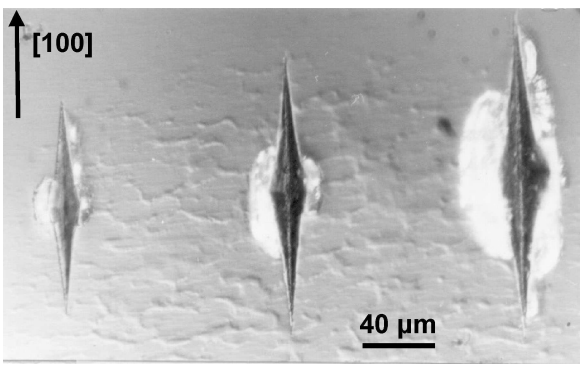

Figure 4. Knoop hardness impressions made using (from left to right) 15 g, 25 and 35 g loads. The longer diagonals of the indentations are aligned parallel to the [100] direction.

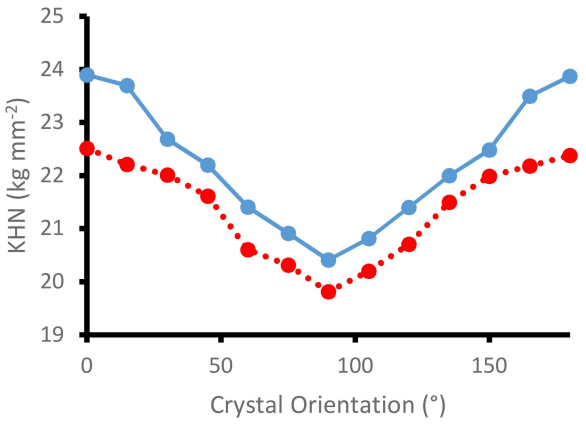

Figure 5. The variation in KHN with crystal orientation made using a 15 g load at temperatures of 295 K (**blue** solid line) and 323 K (**red** dotted line).

occur on the most closely packed planes, for which the interplanar spacing is greatest, in the direction of the shortest unit Burgers vector.

TNT crystallises in the primitive monoclinic space group $P2_1/a$, with unit cell dimensions $a_0 = 1.4911$ nm, $b_0 = 0.6034$ nm, $c_0 = 2.0882$ nm and $\beta = 110.36°$. The {001} planes have the largest interplanar spacing and on the basis of the model {001} probably corresponds to the preferred slip plane. This proposal is supported by the current observation of easy fracture in this plane which reflects low inter-planar forces.

The shortest lattice translation contained in this plane lies in the [010] direction. Therefore the likely slip system is considered to be {001}[010]. The magnitude of the ERSS depends solely on the orientation of the indenter with respect to the operative slip system. The variation in ERSS with indenter orientation was calculated for {001}[010] slip using both the expression derived by Daniels and Dunn and the modified equation of Brookes et al. and the results are shown in Figure 6.

It has also been demonstrated that the Vickers hardness can be related to the ERSS developed beneath the indenter analogously to the models already described for Knoop hardness. In general however the variation in VHN is usually less pronounced and the model less successful in predicting the observed hardness anisotropy on certain faces than in the case of the Knoop indenter. The ERSS values calculated for both the orientations examined and for the {001}[010] slip system using the equations of Daniels and Dunn and Brookes et al. are given in Table 1.

For single crystals, the Vickers hardness generally varies with orientation in a given surface, depending on the orientation of the indenter with respect to the active slip system. Depending on which equation is used, the calculated ERSS for indentation at 45° to the [010] direction is approximately one half (Daniels and Dunn) or one third (Brookes et al.) greater than the value obtained for indentation parallel to this direction. Therefore differences in VHN with orientation should result. However within experimental error, the present measured hardness is the same for both orientations.

This discrepancy between the hardness predicted by the ERSS model and the observed hardness probably results from the extensive cracking which accompanies all Vickers indentations in this material. The ERSS model is only valid for those cases in which the deformation is accommodated by plastic flow. The formation of cracks around the indentation represents a modification in the mode of deformation which results in an apparent increase in hardness; the energy normally directed towards producing dislocation slip being lost in crack generation.

For indentations at 45° to [010] a greater proportion of the indenter pressure is utilised in brittle fracture as compared with indentations at the other orientation. This may compensate for the higher value of ERSS and lead to the production of two indentations of roughly the same size and therefore VHN.

In order to form a crack it is necessary to break the bonds which bind the molecules of the crystal together. Therefore cracking is most likely to occur along crystallographic planes which are held together by only weak intermolecular forces. A projection of the crystal structure of TNT viewed along the [010] direction is shown in Figure 7.

Two potential planes of easy cleavage can be identified corresponding to (001) and (100), in agreement with the observed major crack orientations. In fact crystals of this material can be fairly easily cleaved on {001} planes using a

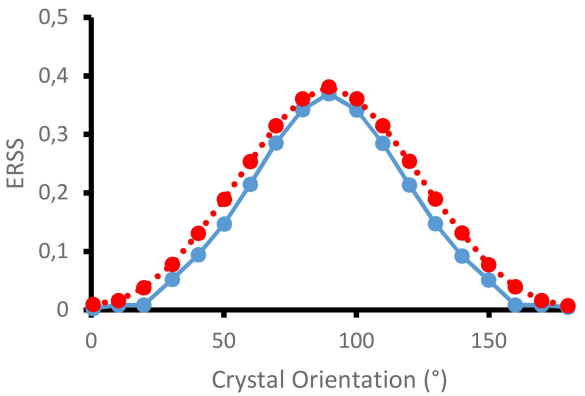

Figure 6. The variation of ERSS with crystal orientation for the {100}[010] slip system after Daniels and Dunn (**blue** solid line) [3] and Brookes et al. (**red** dotted line) [4].

Table 1. The variation in ERSS for TNT (100) faces with Vickers indenter orientation.

	Effective Resolved Shear Stress	
Indenter Orientation to [010]	Daniels & Dunn	Brookes et al.
0°	0.0840	0.1289
45°	0.1737	0.1737

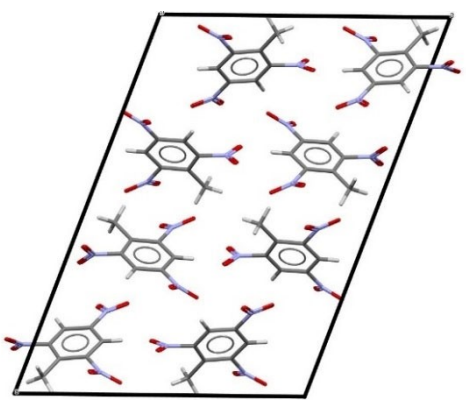

Figure 7. The crystal structure of TNT projected along [010].

sharp razor blade. No special reason can be suggested for the cracks which propagate from the corners of the indentation along the direction at 45° to [010]. However these cracks only appear when the indenter is oriented with its diagonals parallel to this direction. In this case the indenter may be acting as a simple wedge. The cracks follow an irregular path which suggests that their orientation is not particularly associated with a plane of easy separation. The distorted shape of both Vickers indentations (Figure 2) is a direct consequence of the anisotropy of plastic flow. As the indenter penetrates the crystal surface, flow occurs more easily along [100], leading to a piling-up of the material in this direction, whatever the orientation of the indenter.

In the absence of direct evidence concerning the nucleation and mobility of dislocations during indentation, the explanation for the observed independence of VHN from defect density can only be speculative. Previous studies of growth induced defects in TNT by X-ray topography [24] have shown very little evidence for dislocation motion, although the majority of dislocations were observed to lie on the currently postulated slip plane. The lack of dislocation glide was attributed to pinning of the potentially glissile dislocations by impurities. Since the growth dislocations are immobile they cannot take part in plastic deformation. Hence the observed independence of hardness from initial dislocation density can be accounted for by the sessile nature of the growth dislocations. The deformation patterns associated with Vickers indentations and the hardness curves obtained using the Knoop indenter show mirror symmetry about the [100] direction. This is consistent with the two-dimensional point group in TNT projected on {001}. The severe cracking which occurs with the Vickers indenter at all loads makes it less suitable for the study of the plastic properties of this solid than the Knoop indenter which produces hardness impressions almost entirely free from fracture at lower loads.

Both the calculated ERSS curves for Knoop indentation are in excellent agreement with the experimentally determined hardness anisotropy and support the choice of slip system based on structural considerations. Although the two curves are very similar, the variation in ERSS calculated using the equation of Brookes et al. shows better correspondence with the experimental data than that of Daniels and Dunn in the region around [010]. This similarity suggests that, as claimed by the authors, it is more useful in explaining variations in hardness. Other potential, but geometrically less favourable slip directions also exist (particularly [110], [120] and [210]) however no agreement between experiment and theory could be achieved with these systems, implying that the only active slip system is {001}[010].

The analysis of either slip steps or dislocation etch pit arrays following indentation have previously been used as additional evidence to support postulated slip systems. For TNT however, indentation does not produce surface steps and subsequent etching of the hardness impressions fails to reveal the rosette patterns typical of the intersection of mechanically induced dislocation loops with the surface. Both these features are consistent with slip taking place on {001}, since these planes lie parallel to and do not intersect the surface under examination. Up to the present time it has proved impossible to identify slip dislocations around the indentation by X-ray topography. Due to their localised nature the images are masked by the strained region that develops around the indentation mark.

The decrease in hardness observed at the higher temperature is small, but significant. As the temperature is raised, the degree of intermolecular bonding is reduced by thermal expansion of the lattice. The resulting increase in dislocation mobility lowers the resistance to deformation and thus the hardness. Any changes in the operative slip system or in the mode of deformation would be reflected in the nature of the Knoop hardness anisotropy. The fact that at 323 K the shape of the hardness curve is unaltered indicates that there is no change in active slip system up to this temperature.

All pyramidal indenters produce geometrically similar indentations having identical strain fields, irrespective of their size. Consequently the measured hardness is independent of the size of the impression and therefore, should be constant with increasing load.

As the pressure, P, beneath the indenter, $P = F/A$, where F is the force of indentation and A is the cross-sectional area of the indenter, a plot of ln (L) against ln (d), where L is the applied load and d is the size of the indentation, should result in a straight line of gradient 2. The results for TNT (ESI S3) of $n = 2.03(2)$ for [010] and $n = 1.94(2)$ for [001] confirms the independence of VHN from load and indicates that TNT behaves as a classical elasto-plastic solid in the hardness range tested.

4 Conclusion

Microindentation hardness testing on {001} faces was used to determine the hardness of TNT as a function of indenter orientation, indenter load, crystal perfection and temperature.

The VHN was determined to be 22.5 $kg\,mm^{-2}$ at 295 K and was independent of the orientation of the indenter and the perfection of the crystal, in contrast, the KHN varied with indenter orientation in the range 20.5–24.0 $kg\,mm^{-2}$ at ambient temperature. The hard and soft directions were found to lie along the [010] and [100] crystallographic directions respectively. In addition to this, the variation in Knoop hardness was found to be independent of load within the range 15–50 g.

The Knoop hardness anisotropy curve retained the same shape at 323 K, although the overall hardness decreased, indicating that there was no change in deformation mechanism up to this temperature. The decrease in hardness was

attributed to a decrease in intermolecular bonding due to thermal expansion of the lattice.

The dominant operative slip system was determined to be {001}[010] by comparison of the Knoop hardness curve with a theoretical model based on resolved shear stress.

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Data Availability Statement

Data available on request from the authors

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