

Normal Vibrations of Trinitro Toluene: Need for a Fresh Study

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ABSTRACT

In view of certain infirmities in the available data on the normal coordinate analysis of TNT, a fresh study from both theoretical and experimental viewpoints has been necessitated. Wilson's GF matrix method with Urey-Bradley force field has been used to calculate normal frequencies. Valence charge distribution using INDO/MO calculations lend support to the force field used. The experimental data have been obtained from the Fourier transform infrared absorption spectra. This spectrum is a superposition of the two types of molecular structures present in TNT. The changed valence charge distribution in trinitrobenzene on the introduction of the methyl group is indicated as a possible reason for the explosive nature of TNT.

1. INTRODUCTION

Studies on the vibrational spectra of secondary explosives have been reported by several workers¹⁻³ to understand their dynamical behaviour. Boutin *et al*¹ have used the ratio of internal to external energy as a measure of impact sensitivity (2kg/wt for TNT). These measurements are mostly confined to low frequency regions.

One of the authors has reported earlier a detailed study of the normal modes of vibrations of tri amino trinitrobenzene². In continuation of this work, we report, in the present communication, an experimental and theoretical study of the vibrational spectra of trinitrotoluene (TNT), which is one of the most commonly used explosives. In addition to this, we also report the calculations on valence charge distribution, principal polarisabilities and dipole moments. In a recent publication, Nash *et al*⁴ have reported the infrared spectra of TNT and its deuterated analogues recorded in the solid state. In spite of the fact that it is the best work so far, it suffers from several infirmities, e.g. the authors have assumed the structure of TNT to be symmetric belonging to the C_{2v} point group which it is not, as revealed by the recent neutron diffraction studies of Gerard and Hardy⁵. In fact, the asymmetry

is too large to be ignored. Further, Nash *et al* have used a semi-empirical force field whereas in the present communication the Urey-Bradley force field used takes into account 1-3 and 1-4 nonbonded interactions in addition to bonded interactions. Moreover, the frequency assignments for the various functional groups and NO_2 group, in particular, result in a divergence between the experimental and calculated values up to 37 per cent, as acknowledged by the authors⁴ themselves. In view of these facts, it was considered necessary to undertake a fresh and more exhaustive study of the normal modes of vibration of TNT. Our present calculations provide an agreement ranging from 91 to 99 per cent between the observed and calculated frequencies.

2. EXPERIMENTAL DETAILS

The TNT was supplied by ERDL, Pune and the spectra were run on 1800 Perkin Elmer FTIR spectrophotometer equipped with a L- alanine-doped deuterated triglycine sulphate (DTGS) detector, a resistance heated wire as a source and a GE/KBr and mylar beam splitter. The spectra were obtained at 2 cm^{-1} resolution in the range $500\text{-}4000\text{ cm}^{-1}$ and $500\text{-}200\text{ cm}^{-1}$ and are shown in figures 1(a) and 1(b) respectively.

Apodization was carried out by using the triangular function; this resulted in the sacrifice of a little resolution, particularly in the low frequency region. However, this was compensated by running the derivative and difference spectra. As a precaution nujol mull was used to avoid grinding with KBr to form pellets.

3. THEORY AND COMPUTATION METHODS

The well known Wilson's G-F matrix method⁶ with Urey-Bradley force field has been used to evaluate the normal mode frequencies of vibrations. These are given by the eigen values λ of the secular equation $GFF = \lambda L$, where $\lambda = 4\pi^2 C^2 v^2$.

The potential energy is represented as

$$V = \sum_{jk} K'_{jk} r_{jk} (\Delta r_{jk}) + \frac{1}{2} K_{jk} (\Delta r_{jk})^2 + \sum_{ijk} H'_{ijk} r_{ij} r_{jk} (\Delta \phi_{ijk}) + \frac{1}{2} H_{ijk} r_{ij} r_{jk} (\Delta \phi_{ijk})^2 + \sum_{ijk} F'_{ijk} q_{ik} (\Delta q_{ik}) + \frac{1}{2} F_{ik} (\Delta q_{ik})^2 + \sum_j K_j^{\omega} (\Delta \omega_j)^2 + \sum_j K_j^t (\Delta t_j)^2$$

where Δr_{jk} , $\Delta \phi_{ijk}$, $\Delta \omega_j$, Δt_j are the internal coordinates corresponding to bond stretch, angle bend, out-of-plane deformation and torsion respectively.

The potential energy distribution in the j^{th} internal coordinate for the i^{th} normal mode is given by

$$(PED)_j^i = \frac{L_{ji} L_{ji} F_{ji}}{\lambda_i}$$

Molecular orbital calculations have been carried out using CNDO/2 method⁷. In normalizing the molecular orbitals

$$\Psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu}$$

overlap integrals between different atomic orbitals ϕ_{μ} are neglected.

The total electron density for valence electrons is written as

$$\rho = \sum_{\mu\nu} Q_{\mu\nu} \phi_{\mu} \phi_{\nu}$$

where $Q_{\mu\nu}$ is the charge density bond-order matrix defined by

$$Q_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{i\mu} c_{i\nu}$$

In this, the summation extends over occupied molecular orbitals. The diagonal elements of this matrix gives the total charge associated with the atomic orbitals ϕ_{μ} . The total charge density assigned to an atom A is given by

$$\rho_{AA} = \sum_{\mu}^A \rho_{\mu\mu}$$

where the sum is to be taken over all valence atomic orbitals belonging to an atom A. Dipole moments and molecular polarizability have been calculated by atom dipole interaction model⁸.

4. RESULTS AND DISCUSSION

The structure of TNT as reported by Gerard and Hardy⁵ consists of two independent molecules I and II (Fig. 1) which are nearly parallel along the c axis and make a herringbone pattern. The molecule belongs to the monoclinic space group $P_{2_1}c$ with $a = 21.268(9)$, $b = 6.089(1)$, $c = 15.020(7)$ Å. The two molecules are appreciably different in terms of bond lengths and bond angles. The molecules are connected together through hydrogen bonds. Because of intramolecular asymmetry and the existence of two structural forms, the solid state spectra have to be interpreted as arising from both of these molecules. The spectra in the range of 4000-500 and 500-200 cm^{-1} are shown in Fig. 2. Use of symmetry considerations for classification of normal modes is certainly inaccurate. There seems to be no choice but to use the method of brute force to evaluate the modes. Since there are 21 atoms, the total number of normal modes of vibration excluding rotations and translations is 57. The force constants used were first transformed from similar and related molecules such as RDX and TATNB, and later refined to give the best fit with the observed values of frequency. The assignments were made on the basis of normal mode calculations, potential energy distributions, line intensity and line profile.

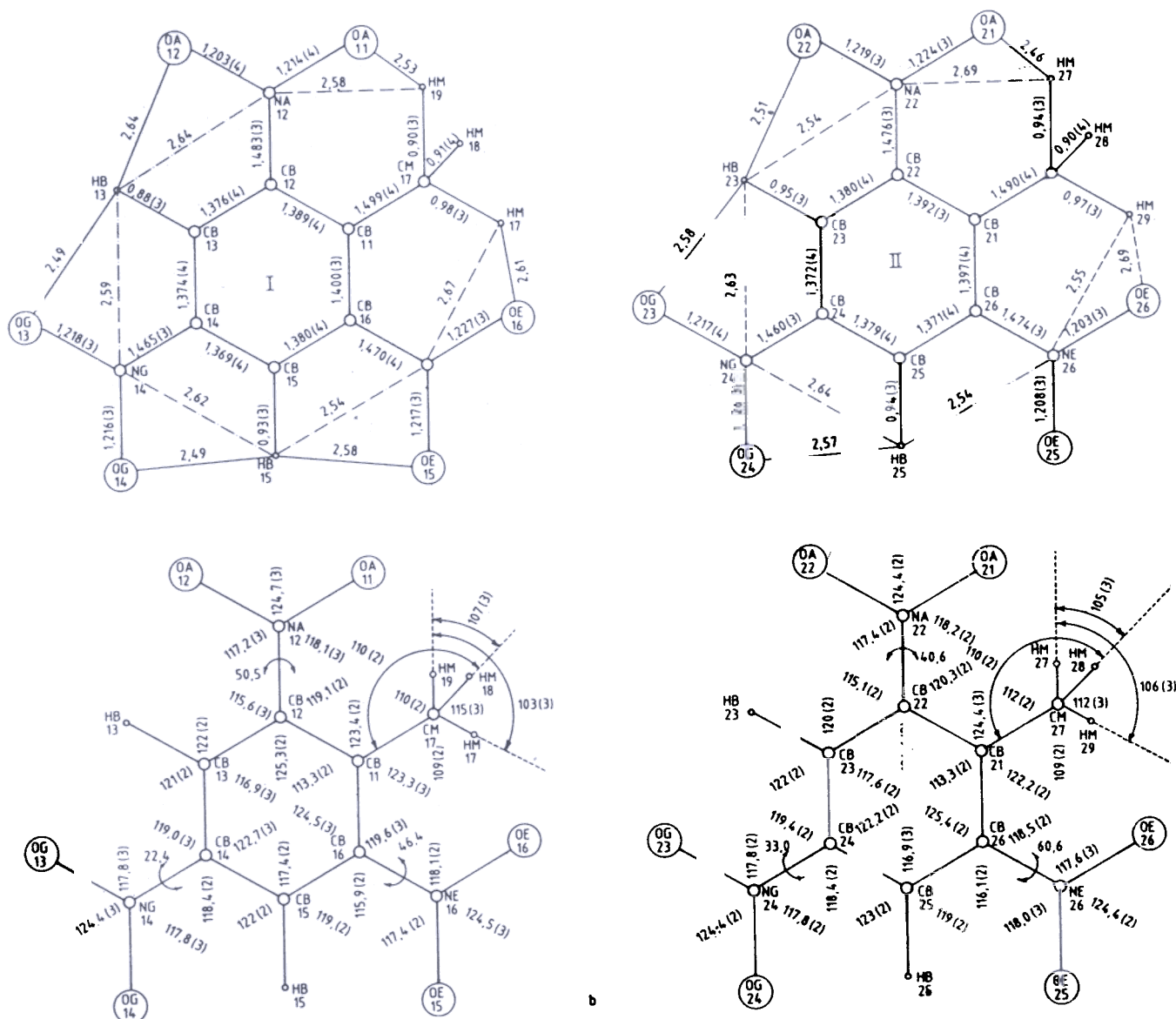


Figure 1. TNT I and II (a) Structure, and (b) Superposition of structures.

4.1 NO_2 Group Frequencies

NO_2 group symmetric and antisymmetric stretch frequencies (shown in Table 1) have been observed in the narrow range of $1338\text{--}1355\text{ cm}^{-1}$ and $1510\text{--}1555\text{ cm}^{-1}$ respectively in para substituted nitrobenzene derivatives⁹. A shift towards lower frequencies is a result of strong hydrogen bonding in the molecule¹⁰. Such a situation is also seen in the case of *O*-nitrophenol, where ν_s falls to 1320 cm^{-1} . A study of a series of multiply substituted nitrobenzene compounds shows that the bands corresponding to the NO_2 stretch appear in the IR spectrum with fairly large intensity. The band at

1353 cm^{-1} corresponds to the symmetric NO_2 stretch. The calculated value for the same is 1344 cm^{-1} (Table 1). In 1,3,5-TNB the asymmetric NO_2 stretching mode appears at 1557 cm^{-1} while 1,2,3-TNB has two bands at 1558 and 1572 cm^{-1} . The nondegenerate and degenerate ν_{as} (NO_2) bands in our calculations are obtained at 1528 cm^{-1} and 1647 cm^{-1} respectively. The observed frequencies corresponding to these modes are 1539 cm^{-1} and 1653 cm^{-1} respectively. The latter frequency has a large mixing of modes with the *C*-*C* stretch. The effects of hydrogen bonding in the case of stretching frequency results in a shift to lower frequency

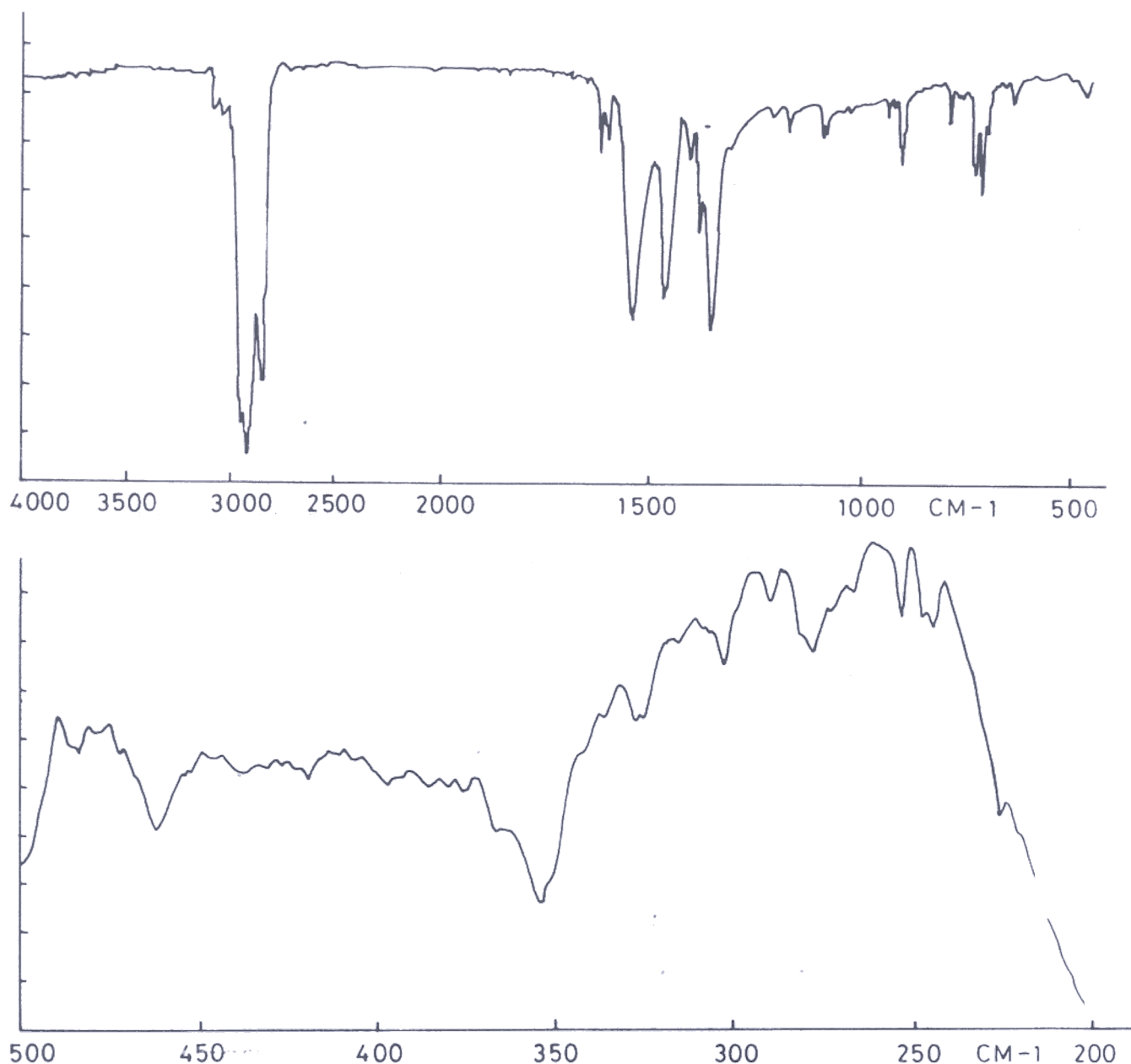


Figure 2. (a) FTIR spectrum of TNT 4000-500 cm^{-1} , and (b) 500-200 cm^{-1} .

and an increase in intensity. However, there is a shift to higher frequencies for bending vibrations accompanied by a small change in intensity. The band at 751 cm^{-1} has been assigned to the totally symmetric *O-N-O* bending mode. In most of the nitrobenzene derivatives it occurs in the range 625-682 cm^{-1} . The shift towards somewhat higher frequencies is due to hydrogen bonding¹¹. The out-of-plane wagging mode of the NO_2 group is expected to have a higher frequency than the bending mode because (a) the moment of

inertia of the group about an axis perpendicular to its plane is much greater than that about an axis in its own plane, and (b) the repulsion in the potential energy function for out-of-plane mode is probably greater than that for the in plane mode. The IR band at 639 cm^{-1} is assigned to the out of plane wagging mode of the oxygen atoms of the nitro group. NO_2 torsional mode appears at 139 cm^{-1} in nitrobenzene and our calculations show it at 115 cm^{-1} .

Table 1. NO₂ Group frequencies

Mode	Present Work			Nash, <i>et al</i> ¹		
	ν_{cal}	ν_{obs}	% diff	ν_{cal}	ν_{obs}	% diff
Symmetric stretch	1344	1353	0.66	1817	1356	33.9
				1813	1356	33.7
				1812	1356	33.6
Asymmetric stretch	1528	1539	0.78	2116	1541	37.3
	1647	1653	0.36	2108	1541	36.7
				2107	1541	36.7
Bend	751	768	2.20			
Wag	692	760	8.90			
	636	639	0.46	655	639	2.50
	610	565	7.90			
Torsion	115					

4.2 CH₃ Group Frequencies

The methyl group has two fundamental stretch frequencies in molecules with C_{3v} symmetry but this increases to three when the symmetry is C_s due to the removal of degeneracy of the ν_{as} vibration. In consequence of it, a series of bands appear between 2980 cm⁻¹ and 2700 cm⁻¹, which vary in position and in intensity depending upon the position of the overtone absorptions. Toluene, the C_s type compound has been studied in detail by several workers¹²⁻¹⁴. This compound shows five bands at 2979, 2952, 2921, 2869, and 2734 cm⁻¹. The band at 2921 cm⁻¹ is the symmetric stretching mode and the weak band at 2734 cm⁻¹, the overtone of the symmetric methyl deformation. Our calculations

assign the bands at 3064 cm⁻¹, 3043 cm⁻¹, and 2983 cm⁻¹ to the symmetric C-H stretch of the methyl group. (Table 2). The asymmetric H-C-H bending mode of the methyl group has been calculated at 1410, 1404, and 1377 cm⁻¹. The symmetric methyl deformation band occurs in toluene at 1381 cm⁻¹. Our calculations give it at 1300 cm⁻¹. The frequency corresponding to the ring C-methyl C torsional mode is calculated to be 1015 cm⁻¹ and is observed at 1026 cm⁻¹.

4.3 Ring Frequencies

The ring C-H stretch frequency as calculated is 3074 cm⁻¹ and is observed at 3084 cm⁻¹ (Table 3). The asymmetric ring C-C stretch is calculated at 1647 cm⁻¹

Table 2. CH₃ Group frequencies

Mode	Present Work			Nash, <i>et al</i> ¹		
	ν_{cal}	ν_{obs}	diff	ν_{cal}	ν_{obs}	% diff
H-C-H Symmetric stretch	3064	3054	0.32	3382	3057	10.6
	3043	2955	2.90	3269	2955	10.6
	2983	2925	1.90	3264	2880	13.3
Asymmetric H-C-H bend	1410	1405	0.35			
	1404	1405	0.07	1515	1437	5.4
		1378	0.07			
Symmetric H-C-H bend						
C-C-H bend	1184	1170	1.19	1221	1171	4.2
				1126	1086	3.7
				1096		
Torsion	1015	1026	1.07	1064	1026	3.7

Table 3. Ring frequencies

Mode	Present Work			Nash, <i>et al</i> ⁴		
	ν_{cal}	ν_{obs}	% diff	$\bar{\nu}_{cal}$	ν_{obs}	% diff
C-H stretch	3074	3084	0.32	3384	3087	9.62
C-C stretch	1647	1653	0.36	1718	1619	6.11
C-C-H bend	1184	1170	1.19			
	1088	1086	0.18	1237	1031	19.9
Wag (H)	1015	1026	1.07	1064	1026	3.7
Torsion	1018			1014		
	1015	1026	.07	1064	1026	3.7

and observed to be 1653 cm^{-1} . The C-C-H bending modes are calculated to be 1184 cm^{-1} and 1088 cm^{-1} with the observed values at 1170 cm^{-1} and 1086 cm^{-1} respectively. The wagging modes of ring hydrogens have been found to lie at 1026 cm^{-1} and have been calculated as 1015 cm^{-1} . Ring C-C torsional modes lie at 1018 cm^{-1} and 1015 cm^{-1} . The close agreement between the observed and calculated frequencies bears testimony to the accuracy of our calculations and assignments.

A comparative study of the principal polarizabilities of benzene, nitrobenzene, dinitrobenzene, TNB and TNT reveals that the polarizability increases gradually on the addition of the nitro groups to benzene, but on the addition of the methyl group to TNB, the principal polarizability suddenly increases from 5.4 for TNB to 40.3 for TNT (Table 4). This clearly indicates that it is the methyl group which gives TNT its highly polarized character and should be in some way responsible for the explosive nature of TNT.

Table 4. Comparative study of the principal polarizabilities

Compound	Principal Polarizabilities		\bar{A}^3 z
	x	y	
Benzene	12	12	3
Nitrobenzene	35	27	4
Dinitrobenzene	39	30	4.6
Trinitrobenzene	38	38	5.4
Trinitrotoluene	59	51	40.3

Electronic charge distribution obtained from molecular orbital calculations can be easily and realistically divided into contributions on individual atoms which may then be compared with qualitative discussions⁷.

On comparing the charge distributions of TNB and TNT, one finds that on the introduction of the methyl group the N-atoms lose some more of their charge which is gained by the C-atom of the methyl group. The highly unstable environment of the methyl group is further destabilized by the presence of an electropositive C-atom in the vicinity of the nucleophilic nitro group. Some recent studies on the relationship between impact sensitivity and molecular electronic charge^{15,16} have shown that two types of parameters are necessary for this relationship. First one is of a 'global' nature, i.e. related to the whole molecule and the other is a local quantity, i.e. the one which relates specifically the 'trigger linkage'. In the present context the ring modes including the motion of the methyl group play the role of the global quantity whereas the sucked charge on C-CH₃ and the neighbouring NO₂ groups is the trigger quantity. Mention may be made of the sensitive modes at 303 cm^{-1} in TNT, 411 cm^{-1} and 360 cm^{-1} in β HMX and 235 cm^{-1} , 212 cm^{-1} in RDX. These modes are capable of generating instability of the molecule when there is an energy input. It has recently been brought to our notice that there is a reverse trend of thermal and impact sensitivities in TNT and TNB, for example TNT is less sensitive than TNB impactwise but the thermal ignition of TNT occurs at a much lower temperature than TNB. This could well be possible because during impact TNT offers larger number of degrees of freedom for energy balance or imbalance. However, during thermal ignition the instability of the system is further aggravated. Hence given a conducive environment, a possible mechanism of explosion would be the vigorous reaction between the methyl group and the adjoining nitro group. During explosion, TNT does not react with any other compound but undergoes a

violent disintegration, the end products being formed by the atoms constituting the molecule. Further, there is no significant difference between the charge distributions of TNT I and TNT II, hence the explosive mechanism is the same for both the molecules.

A preliminary calculation shows that the charge distribution agrees with force constants derived from potentials like Lennard-Jones potential. A detailed study showing its agreement with the Urey-Bradley force field will be published later.

On taking into account the 1-4 nonbonded interactions, no significant effect was observed on the frequencies; hence they were not considered for the final analysis.

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