

TEX: The New Insensitive High Explosive

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ABSTRACT

Insensitive high explosive 4, 10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo (5.5.0.0.^{5,9}0^{3,11}) dodecane (TEX) has been synthesised by an improved laboratory-scale process using 93 per cent to 96 per cent nitric acid as nitrating agent. Characterisation of the product was done based on its physical constants, infrared, differential thermal analysis, and mass spectral studies. Explosive and ballistic parameters of TEX containing formulations were computed using Becker-Kistiakowsky-Wilson (BKW) code and NASA Chemical Equilibrium Composition-71 programme, respectively. Semi-empirical quantum mechanical calculations using the parametric model 3 (PM3) method have been carried out for the TEX molecule. The optimised geometrical parameters and heats of formation were obtained from semi-empirical PM3.

Keywords: Insensitive high explosives, TEX, thermal stability, high energy materials, NTO, 3-nitro-1, 2, 4-triazol-5-one, double-base propellants, DTA, parametric model 3, velocity of detonation, synthesis

1. INTRODUCTION

High performance of explosives usually is vexingly accompanied by their high sensitivity towards external stimuli. This restrictive influence of sensitivity in the pursuit of newer explosives is being addressed to recently. Rather than settling for a compromise between performance and sensitivity, efforts have been made to develop insensitive high explosives. Due attention is also being paid in this context to the thermal stability of potential explosives. In other words, developing explosives having high performance, high thermal stability and insensitivity towards external stimuli are being pursued vigorously.

3-Nitro-1, 2, 4-triazol-5-one (NTO)¹ and 4, 10-dinitro-2, 6, 8, 12-tetraoxa-4, 10-diazatetracyclo (5.5.0.0.^{5,9}0^{3,11}) dodecane² (TEX) are two such important molecules reported recently. Amongst the several high energy materials attempted, TEX finds a unique place with a combination of insensitivity, high performance and density (Table 1).

The paper reports the improved synthesis, properties and theoretically computed structural parameters of TEX. Explosive and ballistic parameters of TEX, and a probable TEX-incorporated propellant formulation has also been discussed.

Table 1. Comparative characteristic properties of insensitive high explosives and RDX

| Explosive | Density (g/cm ³) | VOD (m/s) | ΔH _f (kcal/mol) | Thermal stability (°C) | Impact sensitivity (cm) | Ref |
|-----------|---------------------------------|--------------|-------------------------------|------------------------------|-------------------------------|-----|
| TEX | 1.99 | 8665 | -106 | 285 | >177 | 4 |
| NTO | 1.93 | 8500 | -130 | 252 | 92 | 4 |
| TATB | 1.93 | 8100 | -37 | >310 | 300 | 9 |
| RDX | 1.82 | 8750 | +15 | 220 | 30 | 4 |

2. EXPERIMENTAL PROCEDURE

2.1 Materials

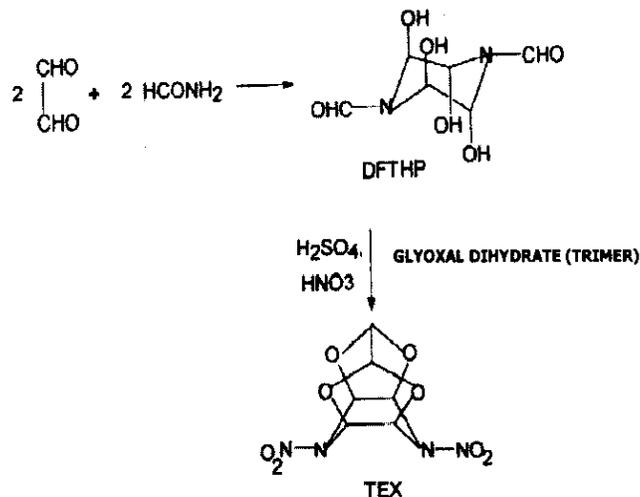
Analytical grade aqueous glyoxal (40%), formamide, sodium bicarbonate, sulphuric acid, glyoxal dihydrate (trimer) and ethyl alcohol were obtained from trade and nitric acid (98%) from Ammunition Factory, Khadki, Pune, and were used without further purification.

2.2 Methodology

IR spectra were recorded on a Perkin-Elmer FTIR-1600 spectrophotometer using KBr matrix. Differential thermal analysis (DTA) curve was obtained on a locally fabricated equipment. The heating rate employed was 10 °C/min and the mass of the sample was 10 mg. The DSC curve was recorded on a Perkin-Elmer DSC-7 instrument under the same conditions. The mass spectrum of the sample was recorded using a Finnigan MAT 1020 automated GC-MS. The impact sensitivity of TEX was carried out on an impact sensitivity apparatus of the fall hammer (2 kg) type. The friction sensitivity was measured using a Julius Peter friction sensitivity apparatus.

2.3 Synthesis of TEX

TEX was synthesised from inexpensive starting materials in two steps, viz., (i) preparation of 1, 4-diformyl-2, 3, 5, 6-tetrahydroxypiperazine (DFTHP), and (ii) cyclisation of DFTHP followed by nitration (Scheme 1).



2.3.1 Preparation of DFTHP

To a stirred aqueous 40 per cent glyoxal solution (145 ml), commercially available formamide (80 ml) was added dropwise over a period of 20 min. The pH of the reaction mixture was adjusted to 8 by adding 40 mg sodium hydrogen carbonate at 25 °C. After 15 min, diformamidoethanediol (DFED) started precipitating out. The reaction was continued (with stirring) for 6 hr. During this period, DFED formed reacted with available glyoxal in the reaction mixture to yield DFTHP. The reaction mixture was then allowed to stand for 25 hr at room temperature with occasional stirring. The product was filtered, washed with cold water and methanol to obtain a milky white product. Yield: 73.6 g (81%); mp: 190 °C (decomposition).

Since DFTHP undergoes slow decomposition after about 6 days of its synthesis, it is recommended that DFTHP synthesised be immediately utilised (within three days) for the synthesis of TEX.

2.3.2 Synthesis of TEX using Solid Glyoxal Dihydrate Trimer

To a cooled solution of sulphuric acid (930 ml), a homogeneous mixture of glyoxal trimer dihydrate (76 g) and DFTHP (150 g) were added at 5 °C with constant mechanical stirring over a period of 20 min. The temperature of the reaction mixture rose by 3 °C during addition. The light brown viscous solution obtained was stirred for 5 hr at

15 °C. Subsequently, the reaction mixture was cooled to 5–7 °C, and commercially available nitric acid (93–96 %, 980 ml) was added dropwise to it over a period of 85 min. During this period, the viscous light brown solution was converted into a less viscous, colourless solution with separation of a small quantity of TEX. The reaction mixture was allowed to stand for 35 hr at room temperature with occasional stirring. The reaction mixture was then quenched by pouring it on crushed ice with stirring to obtain fine white particles of TEX. It was filtered, washed with plenty of ice cold water and aqueous ethanol. Yield: 79 g, (55 %); mp: > 250 °C.

Alternatively, TEX has also been prepared following a route similar to the above, except for the use of 40 per cent aqueous glyoxal in place of solid glyoxal trimer dihydrate, but in low yields (25 %).

3. SCALING UP OF TEX & OPTIMISATION OF REACTION CONDITIONS

Several batches were carried out at 100 g level under different reaction conditions and finally the reaction parameters were optimised and a modified process for TEX was developed. The optimised reaction parameters are presented in Table 2. In a typical 100 g batch, sulphuric acid (1160 ml), a homogeneous mixture of glyoxal trimer dihydrate (95 g) and DFTHP (190 g) were added at 5 °C with constant mechanical stirring over a period of 20 min. Further, the procedure followed was similar to that described in Section 2.3.2.

Table 2. Optimisation of reaction conditions in TEX synthesis

| Parameters | Reported | Modified |
|----------------------------------|----------|------------|
| Reaction time (hr) | 45 | 35 |
| Reaction temperature (°C) | 0 | + 5 to + 7 |
| Nitric acid (%) | 100 | 93 – 94 |
| Addition of H_2SO_4 (ml/min) | – | 4.5 |
| Addition of glyoxal (g/min) | – | 2 |
| Addition of HNO_3 (ml/min) | – | 12 |

Table 3. Parametric model 3 bond lengths (Å) in TEX molecule

| Position of the bond | Bond length (Å) |
|--|-----------------|
| <i>N1-C2, C3-N4</i> <i>C7-N4, N1-C8</i> | 1.497 |
| <i>C2-C3, C6-C8</i> | 1.566 |
| <i>C12-C11</i> | 1.573 |
| <i>C3-O5, C6-O9,</i> <i>C8-O10, C12-O5</i> <i>C11-O9, C11-O10</i> <i>C2-O13</i> | 1.419 |
| <i>N4-N7, N1-N14</i> | 1.517 |
| <i>C2-H15, C3-H16</i> <i>C8-H18, C11-H19</i> <i>C12-H20</i> | 1.114 |
| <i>N14-O21, N14-O22</i> <i>N7-O23, N7-O24</i> | 1.202 |

4. QUANTUM CHEMICAL INVESTIGATIONS

The semi-empirical quantum chemical calculations based on the PM3 method have been performed using the general atomic molecular and electronic structure system (GAMESS) program³. Optimised geometrical parameters thus obtained are presented in Tables 3 and 4. The heat of formation (–106 kcal/mol) thus derived agrees well with the reported one⁴.

Table 4. Parametric model 3 bond angles in TEX molecule

| Position of bond angle (degree) | Bond angle |
|--|------------|
| <i>C2-C3-N1, N4-C2-C3</i> | 112.00 |
| <i>C7-N4-C3, C8-N1-C2</i> | 114.40 |
| <i>O5-C2-C3, O9-C6-C8</i> | 102.80 |
| <i>C6-C8-O10, C3-C2-O13</i> | 118.10 |
| <i>N7-N4-C3, N14-N1-C2</i> | 107.80 |
| <i>C11-O10-C8, C12-O5-C3</i> | 106.46 |
| <i>O21-N14-N1, O22-N14-N1,</i> <i>O23-N7-N4, O24-N7-N4</i> | 113.70 |
| <i>H15-C2-C3, H16-C2-C3,</i> <i>H17-C6-C8, H18-C8-C7</i> <i>H19-C11-C12, H20-C12-C11</i> | 111.00 |

The explosive and ballistic parameters were predicted using molecular formula, density and heat of formation data. The explosive parameters, such as velocity of detonation (VOD), Chapmaan-Jouget (CJ) pressure were computed from Becker-Kistiakowsky-Wilson (BKW) equation of state^{5,6}. Ballistic parameters, such as specific impulse (I_{sp}), mean molecular weight of exhaust gases, etc. were computed using NASA programme^{6,7}. Explosive and ballistic parameters of TEX and TEX containing formulations are presented in Tables 5, 6 and 7.

Table 5. Theoretically computed ballistic parameters of TEX

| Ballistic parameters | Theoretical values |
|---|--------------------|
| Flame temperature (K) | 2160 |
| Mean molecular weight of gases (g) | 23.83 |
| Characteristic velocity (m/s) | 1315 |
| Specific impulse (I_{sp}) (s) | 210 |
| Specific impulse (I_{sp}) in vacuum (s) | 226 |

Table 6. Theoretically computed explosive parameters of TEX

| Explosive parameters | Theoretical values |
|------------------------|--------------------|
| CJ VOD (m/s) | 8749 |
| CJ pressure (kbar) | 365 |
| CJ temperature (K) | 1706 |
| CJ volume (cc/g) | 3.818 |
| Volume of gas (cc/mol) | 11.80 |

Table 7. Comparison of theoretically computed performance parameters of propellant formulations containing RDX/TEX

| Explosive | I_{sp} at 70 kg/cm ² (s) | Characteristic velocity (m/s) | Flame temperature (K) |
|-----------|---------------------------------------|-------------------------------|-----------------------|
| RDX | 221 | 1384 | 2262 |
| TEX | 220 | 1375 | 2280 |

Control composition: Nitrocellulose* (49.5 %); nitroglycerine (30.5 %); carbamite (3.0 %); DEP (7.0 %); RDX/TEX (10.0 %).

*(12.2 % nitrogen)

5. RESULTS & DISCUSSION

The IR spectrum of DFTHP reveals stretching vibration frequencies for CO, OH and C-H at 1670 cm⁻¹, 3324 cm⁻¹ and 2924 cm⁻¹, respectively. The IR spectrum of TEX reveals N-NO₂ stretching vibration frequencies at 1394 cm⁻¹ and 1594 cm⁻¹; C-O-C and C-H, respectively at 1022 cm⁻¹ and 3052 cm⁻¹. The DSC curve of DFTHP shows an initial temperature of decomposition (T_i) at 200 °C. The DTA curve of TEX exhibits T_i at 260 °C and maximum temperature (T_m) at 285 °C. Mass spectrum of TEX indicates the presence of M^{+1} peak at 263 amu and a base peak at 59 amu. Peaks at 216 amu and 170 amu clearly indicate the elimination of both the nitro groups of TEX molecule. Sensitivity data obtained for TEX clearly shows that TEX is insensitive towards impact ($h_{50\%} > 177$ cm) and friction (> 36 kg).

The present method of synthesis is a considerable improvement over the previously reported method² in that TEX is obtained in reasonable yield with the use of commercially available nitric acid (93–94 %). This avoids the tedious method of preparation of 100 per cent nitric acid with which, however, better yield can be realised. In addition, the reaction time and the temperature are also improved in the present method.

The heat of formation (-106 kcal/mol) from the PM3 method matches well with the experimental (-106.5 kcal/mol). It is known that the heat of formation from the semi-empirical PM3 method agrees quite well with those derived from the experiments⁷, typical deviation being 5–8 kcal/mol.

The geometry of TEX optimised at PM3 method is depicted in Fig. 1. The theoretically computed bond lengths and bond angles (Tables 3 and 4) are reported for the first time. It is clear from Table 3 that C-C bonds which are common to the six-membered ring and one of the five-membered rings, namely C2-C3 and C6-C8 are much longer (1.566 Å) than normal C-C bonds observed in a six-membered ring in boat conformation. The explanation for this is the fact that these carbon atoms are attached to more electronegative O and

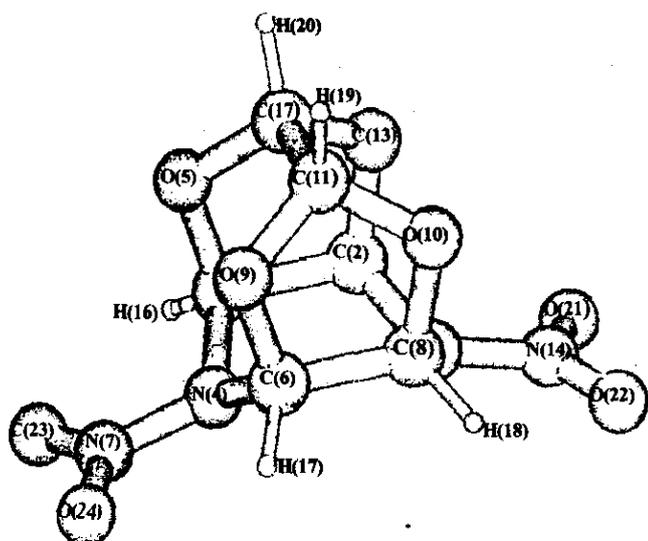


Figure 1. Geometry of TEX optimised at PM3 method

N atoms, the *N* atoms (*N*1 and *N*4), in turn, have strong electron withdrawing NO_2 groups attached to them.

Thus, these *C* atoms (*C*2, *C*3, *C*6 and *C*8) are subjected to large amount of stretching and hence the observed longer bond lengths. The *C*11-*C*12 (Table 3) bond length (1.576 Å) is the longest bond length observed in TEX and is obviously due to the strained configuration of two fused five-membered rings, joined by this bond. Also, these *C* atoms are attached to electronegative *O* atoms [two each; *C*11-*O*9, *C*11-*O*10 and *C*12-*O*5, *C*12-*O*13 (Fig.1)]. The *C*-*O*-*C* bond angle [*C*11-*O*10-*C*8 and *C*12-*O*5-*C*3 (Table 4)] in TEX is computed to be 106.46° which is smaller than normal *C*-*O*-*C* bond angles observed in cyclic ethers, which may be attributed to the strain¹⁰ in the structure. Other bond angles also may be explained on the same lines

The theoretically computed performance of TEX (Table 6) indicates that VOD and blast pressure are at par with RDX. Predicted ballistic parameters of TEX incorporated double-base propellant formulations (Table 7) show that I_{sp} and characteristic velocity are similar to RDX-incorporated double-base propellants.

6. CONCLUSION

An easy and improved method of synthesis of TEX has been developed. The synthesis involves two steps, starting from inexpensive starting materials. Reaction conditions operative in the modified process have been optimised at laboratory scale. The optimised geometrical parameters of TEX have been presented. Ballistic and explosive parameters of TEX and TEX containing propellant formulations have been computed which prove their performance at par with the RDX-incorporated propellant formulations.

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Contributors



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