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# Crystal Structure and Thermal Analysis of 1,4-Di(2,4,6-trinitro-styryl)benzene

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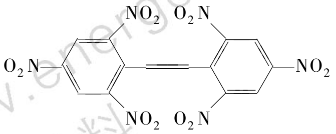
**Abstract**: The synthesis, culture of crystal and single-crystal X-ray crystallography of a new kind of polynitrostilbene [1,4-di(2,4,6-trinitro-styryl)benzene, TNT-TTD], which was synthesized through Knoevenagel Condensation by using piperidine as a base catalyst were reported. The crystal belongs to the Triclinic system with space group $P$-1. The compound was characterized by using FT-IR, $^1$H NMR, $^{13}$C NMR and MS spectroscopy techniques. Density functional theory (DFT) B3LYP was employed to optimize structure and calculate frequencies of TNT-TTD. The calculated geometrical parameters were close to the corresponding experiments ones. The thermal decomposition of the title compound was investigated by DSC and TG-DTG methods at heating rate 10 ℃ · min$^{-1}$. The melting point and initial decomposed temperature of TNT-TTD is 302 ℃ and 311 ℃. The results indicate that TNT-TTD has high heat resistant ability.

**Key words**: organic chemistry; polynitrostilbene; molecular structure; density functional theory; thermal decomposition

**CLC number**: TJ55; O62　　**Document code**: A

## 1 Introduction

During crude oil production, certain explosives are utilized for perforating the source rocks. As the average depths of the wells and, as a consequence the ambient temperatures in the wells are increasing or in applications requiring the explosive to withstand significant temperatures before initiation, heat-resistant explosives are of growing interest for the petroleum industry. Modern explosives have to stand temperatures up to 260 ℃ for some hours without noticeable thermal decomposition [1]. Stilbene is a kind of compounds containing C═C between phenyl ring that can be widely used in medical and energetic materials industry. The typical stilbene, hexanitrostilbene (HNS, Scheme 1) is a common example of this group and is one kind of heat-resistant explosive [2].



**Scheme 1　Structure of hexanitrostilbene**

TNT-TTD is similar with HNS. W. A. Gey[3] et al had studied the linear crystallization of TNT systems and Feng Zeng-guo and Cheng Boren[4,5] had studied the synthesis and characters of some thermal-stable explosives. But they have not obtained their crystal structures. In this work the title compound was synthesized via piperidine catalyzed Knoevenagel Condensation and its single crystal was cultured. The molecular and crystal structures were determined by X-ray single crystal diffraction analysis. The thermal decomposition process of TNT-TTD was investigated in order to examine its thermal stability. A theoretical calculation was also performed by using the DFT method B3LYP with the 6-31G$^{**}$ and 6-311G$^{**}$ basis sets.

## 2 Experimental Section

### 2.1 General

The NMR spectra were determined on a Bruker AV 400 MHz 400 spectrometer. $^1$H and $^{13}$C were operated respectively in DMSO at room temperature. All chemical shifts were reported in δ downfield from tetramethylsilane as an internal standard. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer (KBr pellet) in the range of 4000 - 400 cm$^{-1}$. Elemental analyses were carried out on a Flash EA 1112 full-automatic microanalyser. Mass spectra (MS) in the electronic impact positive ions were obtained with a GCT-MS Micromass spectrometer. Thermal properties of the compounds were measured

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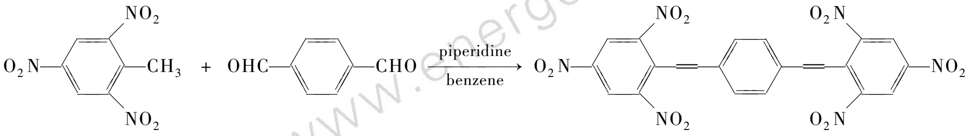
**Biography**: LIU Yan-hong (1976 - ), female, Ph. D. Research field: Physical Chemistry. e-mail: liuyanhong - 2000@163. com using a differential scanning calorimetry (DSC), Perkin-Elmer Pyris-1 DSC under nitrogen atmosphere at a heating rate of 10 ℃ · $\text{min}^{-1}$. A Perkin-Elmer Pyris-1 TG analyzer was used for thermogravimetric analysis. About 0.5 mg of sample was held in a platinum pan, in a flow of dry, oxygen-free nitrogen at 20 ml · $\text{min}^{-1}$, and the heating rate was 10 ℃ · $\text{min}^{-1}$. The structure of the product was determined by single crystal X-ray diffraction.

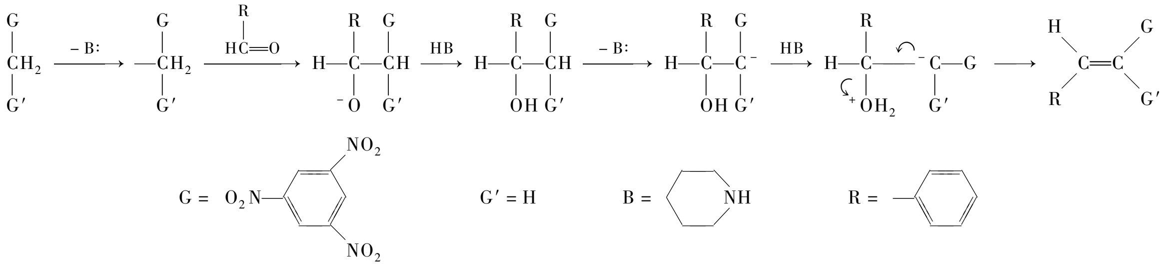
## 2.2 Synthesis

The synthesis of polynitrostilbene (TNT-TTD) was attempted (Scheme 2).

The mechanism of the reaction is showed in the Scheme 3. In this reaction the piperidine was used as the catalyst.



**Scheme 2 The synthesis of polynitrostilbene**



**Scheme 3 The mechanism of the reaction**

The general procedure is illustrated by that for the title compound 2, 4, 6-trinitrotoluene (TNT) (0.04 mmol), terephthalaldehyde (0.02 mmol) and 100 mL benzene were placed into a dry three-neck 100 mL flask equipped with a separate vessel of water and oil, a condenser and a stir bar. 1 mL piperidine was added to the reaction flask as catalyst. The reaction mixture was heated to reflux for 20 h. Then added the ethanol to the flask the resulted dark brown reaction mixture was freezed for 12 h. The mixture was filtrate and purified by acetone. The crystal was cultured in DMF, pale brown, mp 302 ℃. Yield is 70%. $^1$H-NMR (DMSO/TMS) $\delta_H$: 9.12 (s, 2H), 7.6 (s, 4H), 7.59 (s, H), 7.54 (s, 1H), 6.86 (s, 1H), 6.80 (s, 1H), 2.50 (s, 2H). $^{13}$C-NMR (DMSO/TMS) $\delta_C$: 149.54, 146.48, 136.37, 135.88, 132.34, 128.06, 123.04, 119.25; IR (KBr, $\text{cm}^{-1}$): $\nu^{as}_{NO_2}$: 1599, 1536 $\text{cm}^{-1}$, $\nu^{s}_{NO_2}$: 1344 $\text{cm}^{-1}$; —O—$NO_2$: $\nu^{s}_{NO_2}$: 1284 $\text{cm}^{-1}$, $\nu_{C—H}$: 3092 $\text{cm}^{-1}$. $\delta_{C═C}$: 971 $\text{cm}^{-1}$, $\delta_{C—H}$: 924 $\text{cm}^{-1}$, $NO_2$ scissors: 819 $\text{cm}^{-1}$. MS (EI) ($m/z$) 552 (M+, 21); Analysis calculated for $C_{22}H_{12}N_6O_{12}$: C 47.80, H 2.24, N 14.85; Found: C 47.84, H 2.19, N 15.22.

## 2.3 X-Ray crystallography

The structure of the title compound is determined by single crystal X-ray diffraction. Dimensions of the single crystal used for measurement were 0.40 mm × 0.20 mm × 0.16 mm. Cell parameters were determined in the range of $2.29° < \theta < 27.48°$ at the temperature of 293(2) K. 2459 independent reflections were obtained, among which 1521 observed reflections with $I > 2\sigma(I)$ were used for the determination and refinement of the crystal structure in the range of $-10 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$. $C_{22}H_{12}N_6O_{12}$, $Mn = 552.38$, Triclinic, space group $P$-1, $a = 8.230(2)$, $b = 8.627(2)$, $c = 9.587(2)$ Å, $\alpha = 90.23$, $\beta = 109.35(3)$, $\gamma = 117.00(3)°$, $V = 562.5(2)$ Å$^3$, $D_c = 1.631 \text{g} \cdot \text{cm}^{-3}$, $Z = 1$, $F(000) = 282$, $\mu = 0.116 \text{ mm}^{-1}$. The final $R_1 = 0.0476$ (for observed data) and $wR_2$ was 0.1225 (for data $I > 2\sigma(I)$), $R_1 = 0.0731$, $wR_2 = 0.1288$ (for all data). Hydrogen atoms were located by geometric calculation, but their positions and thermal parameters were fixed during the structure refinement.

All calculations are carried out with Sheldrick, G. M. (1998) SHELXS 98 (REF) program [6], for the Solution of Crystal Structure, University of Gottingen, Germany.

# 3 Results and Discussion

## 3.1 Crystal structure of the title compound

The X-ray single crystal structure of TNT-TTD was determined. The bond lengths and bond angles are summarized in Table 1. The unit structure and the packing of the molecule in crystal lattice are illustrated in Fig. 1 and Fig. 2 respectively and the following discussion the numbering of the atoms is given in Fig. 1, which illustrates the experimental geometry of TNT-TTD.

**Table 1 Selected bond lengths, angles and dihedral angels for TNT-TTD crystal structure parameters and theoretical TNT-TTD molecules**

| parameters | experimental data | B3LYP/6-31G* | B3LYP/6-311G** |
|---|---|---|---|
| lengths(Å) | | | |
| O1—N1 | 1.211(2) | 1.229 | 1.222 |
| O2—N1 | 1.207(2) | 1.227 | 1.220 |
| O3—N2 | 1.225(2) | 1.228 | 1.220 |
| O4—N2 | 1.222(2) | 1.222 | 1.221 |
| O5—N3 | 1.220(2) | 1.229 | 1.222 |
| O6—N3 | 1.217(2) | 1.223 | 1.216 |
| N1—C7 | 1.476(2) | 1.481 | 1.488 |
| N2—C9 | 1.480(2) | 1.471 | 1.478 |
| N3—C11 | 1.479(2) | 1.482 | 1.487 |
| C1—C2 | 1.379(3) | 1.383 | 1.380 |
| C1—C3A | 1.402(2) | 1.412 | 1.409 |
| C2—C3 | 1.393(3) | 1.383 | 1.381 |
| C3—C1A | 1.402(2) | 1.407 | 1.404 |
| C3—C4 | 1.469(2) | 1.458 | 1.458 |
| C4—C5 | 1.321(3) | 1.350 | 1.346 |
| C5—C6 | 1.466(2) | 1.463 | 1.463 |
| C6—C11 | 1.404(2) | 1.416 | 1.412 |
| C6—C7 | 1.409(2) | 1.418 | 1.415 |
| C7—C8 | 1.384(2) | 1.390 | 1.387 |
| C8—C9 | 1.378(3) | 1.386 | 1.383 |
| C9—C10 | 1.377(3) | 1.390 | 1.387 |
| C10—C11 | 1.381(2) | 1.385 | 1.382 |
| angles (°) | | | |
| C9—C10—C11 | 117.14(2) | 118.14 | 118.21 |
| C10—C11—C6 | 125.25(2) | 124.21 | 124.14 |
| C10—C11—N3 | 115.06(2) | 114.69 | 114.78 |
| C6—C11—N3 | 119.69(2) | 121.00 | 121.00 |
| O2—N1—O1 | 123.86(2) | 124.86 | 125.22 |
| O2—N1—C7 | 118.16(2) | 116.80 | 116.67 |
| O1—N1—C7 | 117.91(2) | 118.31 | 118.09 |
| O4—N2—O3 | 125.87(2) | 125.58 | 125.75 |
| O4—N2—C9 | 117.52(2) | 117.11 | 117.05 |
| O3—N2—C9 | 116.60(2) | 117.29 | 117.19 |
| O6—N3—O5 | 124.6(2) | 126.15 | 126.31 |
| O6—N3—C11 | 118.30(2) | 117.27 | 117.15 |
| O5—N3—C11 | 117.04(2) | 116.51 | 116.48 |
| C2—C1—C3A | 121.45(2) | 121.05 | 121.09 |
| C1—C2—C3 | 121.04(2) | 121.05 | 121.09 |
| C2—C3—C1A | 117.51(2) | 117.88 | 117.80 |
| C2—C3—C4 | 120.51(2) | 123.63 | 123.62 |
| C1A—C3—C4 | 121.97(2) | 118.48 | 118.57 |
| C5—C4—C3 | 123.66(2) | 126.71 | 126.77 |
| C4—C5—C6 | 130.37(2) | 123.62 | 123.91 |
| C11—C6—C7 | 112.98(2) | 113.94 | 113.96 |
| C11—C6—C5 | 120.93(2) | 122.64 | 122.87 |
| C7—C6—C5 | 126.01(2) | 123.41 | 123.15 |
| C8—C7—C6 | 124.59(2) | 123.51 | 123.55 |
| C8—C7—N1 | 114.10(2) | 114.91 | 114.92 |
| C6—C7—N1 | 121.25(2) | 121.53 | 121.48 |
| C9—C8—C7 | 117.49(2) | 118.67 | 118.65 |
| C10—C9—C8 | 122.42(2) | 121.32 | 121.28 |
| C10—C9—N2 | 119.05(2) | 119.25 | 119.29 |
| C8—C9—N2 | 118.52(2) | 119.41 | 119.42 |
| dihedral angles (°) | | | |
| C3A—C1—C2—C3 | -0.10(3) | -0.08 | -0.07 |
| C1—C2—C3—C1A | 0.10(3) | 0.19 | 0.24 |
| C1—C2—C3—C4 | -178.73(2) | -179.61 | -179.58 |
| C2—C3—C4—C5 | 156.95(2) | 2.41 | 4.66 |
| C1A—C3—C4—C5 | -21.80(3) | -177.39 | -175.16 |
| C3—C4—C5—C6 | 179.33(2) | -178.75 | -178.65 |
| C4—C5—C6—C11 | -155.20(2) | -38.59 | -38.88 |
| C4—C5—C6—C7 | 28.40(3) | 141.61 | 141.37 |
| C11—C6—C7—C8 | 2.50(3) | 1.64 | 1.79 |
| C5—C6—C7—C8 | 179.15(2) | -178.53 | -178.44 |
| C11—C6—C7—N1 | -174.49(2) | 179.59 | 179.85 |
| C5—C6—C7—N1 | 2.20(3) | -0.58 | -0.37 |
| O2—N1—C7—C8 | 63.20(2) | -24.23 | -27.23 |
| O1—N1—C7—C8 | -113.80(2) | 154.76 | 151.78 |
| O2—N1—C7—C6 | -119.50(2) | 157.65 | 154.53 |
| O1—N1—C7—C6 | 63.40(2) | -23.34 | -26.43 |
| C6—C7—C8—C9 | -3.40(3) | 1.59 | 1.47 |
| N1—C7—C8—C9 | 173.78(2) | -176.47 | -176.70 |
| C7—C8—C9—C10 | 0.70(3) | -2.10 | -2.08 |
| C7—C8—C9—N2 | -178.24(6) | 178.27 | 178.29 |
| O4—N2—C9—C10 | -13.20(3) | 0.09 | -0.11 |
| O3—N2—C9—C10 | 166.04(9) | -179.74 | 179.85 |
| O4—N2—C9—C8 | 165.83(8) | 179.71 | 179.51 |
| O3—N2—C9—C8 | -15.00(3) | -0.32 | -0.522 |
| C8—C9—C10—C11 | 2.50(3) | -0.73 | -0.68 |
| N2—C9—C10—C11 | -178.55(2) | 178.87 | 178.93 |
| C9—C10—C11—C6 | -3.50(3) | 4.41 | 4.38 |
| C9—C10—C11—N3 | 176.54(6) | -172.43 | -172.56 |
| C7—C6—C11—C10 | 1.10(3) | -4.74 | -4.80 |
| C5—C6—C11—C10 | -175.76(2) | 175.44 | 175.43 |
| C7—C6—C11—N3 | -178.95(2) | 171.91 | 171.95 |
| C5—C6—C11—N3 | 4.20(3) | -7.91 | -7.81 |
| O6—N3—C11—C10 | -131.50(2) | 120.34 | 120.15 |
| O5—N3—C11—C10 | 47.80(2) | -57.01 | -57.48 |
| O6—N3—C11—C6 | 48.60(3) | -56.61 | -56.90 |
| O5—N3—C11—C6 | -132.20(2) | 125.94 | 125.47 |

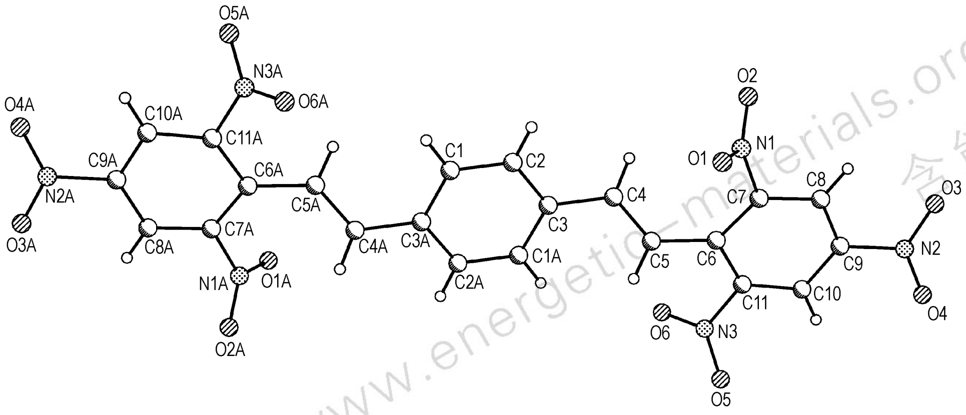


Fig. 1 Molecular structure of TNT-TTD and the numbering atoms

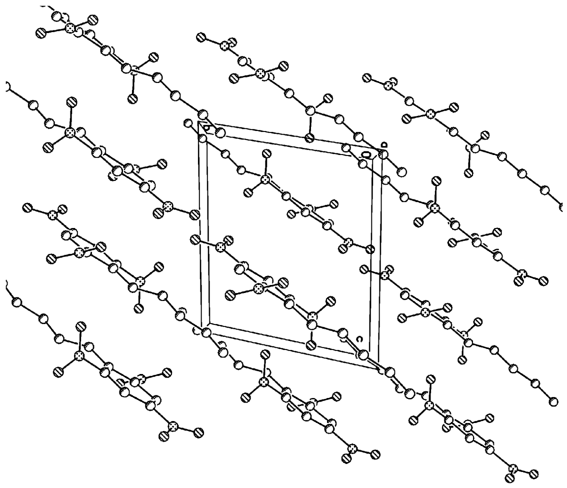


Fig. 2 Crystal packing of TNT-TTD

From the Table 1 and Fig. 1, it is found that the structure is symmetry of center. The results show that C—C bond length of the benzene ring is different to the normal length due to the nitro group and the double bond affect. C8—C9, C9—C10 is shorter than C7—C8, C11—C10 and C6—C7, C6—C11. The length of the C═C bond is the shortest, while the C—N bond length is the largest and is similar to the C—N length in the TNT and larger than the normal C—N length (1.471Å)[7]. The endocyclic angles are also different. In the middle phenyl plane C2—C3—C1A is 117.5°, other angles are 121°. In the side benzene plane C7—C6—C11 (112.9°) is the smallest while C8—C9—C10 (122.4°) is the largest. There is a considerable deformation of the benzene ring for the largest deviation from $sp^2$ angle (120°) is 7.1°, which indicates that there is some torsion in the benzene and the stability of the phenyl plane will be affected. In the crystal structure the bond length of C—N and the angle of O—N—O are largest. The results predict that the C—N bond is easier to split than others. The N2 nitro group is almost coplanar to the benzene ring while the other two-nitro groups are turn away from the plane. This probably subjects to intermolecular forces, such as van der Waals interactions and the repulsion between the groups. It is found that the angles are O2—N1—O1 123.8°, O2—N1—C7 118.2°, O1—N1—C7 117.9°, O6—N3—O5 124.6°, O6—N3—C11 118.3°, O5—N3—C11 117.0°. The data show that the N is $sp^2$ hybrid because the angles of N—O—N and C—N—O are all close to 120°.

## 3.2 Computational study of TNT-TTD

### 3.2.1 Optimized of the structure

With the advance of quantum chemistry method, the structures and energies of the energetic materials can be theoretically predicted in high accuracy. Density functional theory (DFT) method has recently been successfully applied to investigate the structures and predict properties of these compounds, such as TNT[7] and oligomers[8]. Therefore, geometry optimization of TNT-TTD is performed using the B3LYP hybrid density functional theories (DFT)[9, 10] with the 6-31G$^{**}$ and 6-311G$^{**}$ basis sets. Here, B3LYP denotes the combination of the Becke's three-parameter exchange with the Lee-Yang-Parr (LYP) correlation functional. All the electronic structure calculations are carried out by Gaussian 98 program[11].

The DFT calculations give a remarkably wonderful description of the molecular geometry. The calculated data are shown in the Table 1. In the Table 1, the computation results obtained at B3LYP/6-31G$^{**}$ and B3LYP/6-311G$^{**}$ levels of theory are close to the experimental data. All bond distances obtained at B3LYP/ 6-31G$^{**}$ level of theory deviate by less than 0.02Å with experimental values and the largest bond-angle deviation is 6.7°.

In the side benzene ring the three nitro-groups point to different faces. The N2 group is almost coplanar to the benzene ring and the other nitro groups twist away the benzene ring, the optimized twist angles respectively are ~ −57.48°, ~ −27.23°. Also the inner angles of the benzene are about 120°, which is same as the experimental. However there is a distinct difference in the dihedral angels, which involved the double bond and the N1 group. This attributes to the facts that the calculate data are corresponding to the gas phase while the crystal data are about the solid state. The geometry of the solid-state structures is subject to intermolecular forces, such as van der Waals interactions and crystal packing forces.

### 3.2.2 Vibrational analysis

Because the optimized data from the B3LYP method between 6-31G$^{*}$ and 6-311G$^{**}$ basis sets have exiguous distinction and the calculated frequencies at 6-31G$^{*}$ and 6-311G$^{**}$ levels of theory are similar[12], the B3LYP/6-31G$^{*}$ level of theory is selected to calculate the TNT-TTD's Vibrational frequencies. The predicted frequencies and intensities of TNT-TTD are listed in Table 2, where the main absorption positions of some functional groups

**Table 2 The vibrational assignment of TNT-TTD based on the B3LYP/6-31G$^{*}$ frequencies and assignment are presented**

| No. | $\nu$/ cm$^{-1}$ | intensity | assignment |
|---|---|---|---|
| 1 | 556.3 | 14.6 | C—H in plane bend, ring torsion |
| 2 | 713.5 | 32.8 | N—O scissors |
| 3 | 728.5 | 10.2 | C—C bone of the side plane bend |
| 4 | 738.6 | 29.8 | C—C bone of the plane bend |
| 5 | 742.4 | 37.9 | C—C bone of the plane bend |
| 6 | 746.9 | 28.2 | 4 C—N out of plane |
| 7 | 747.9 | 15.8 | C—N out of plane |
| 8 | 753.2 | 17.2 | C—N out of plane |
| 9 | 769.7 | 7.9 | 1,3 C—N out of plane |
| 10 | 790.6 | 5.7 | C—N out of plane |
| 11 | 818.0 | 22.9 | C—C stretch of the middle benzene ring |
| 12 | 829.4 | 139.3 | C—H in the plane bend |
| 13 | 835.2 | 19.2 | C—H in the plane bend |
| 14 | 876.9 | 15.4 | C—C in the plane bend |
| 15 | 892.5 | 49.2 | C—H in the plane bend |
| 16 | 894.6 | 11.8 | C—C stretch of the middle benzene ring |
| 17 | 936.7 | 18.9 | 1,3 C—N stretch |
| 18 | 936.7 | 46.8 | 1,3 C—N stretch |
| 19 | 947.4 | 15.8 | C8—H in the plane |
| 20 | 947.4 | 14.6 | C8A in the plane |
| 21 | 956.4 | 97.2 | C8—H and C8A in the plane |
| 22 | 964.9 | 6.1 | C8—H and C8A out of plane |
| 23 | 965.0 | 13.1 | C8—H and C8A out of plane |
| 24 | 1021.3 | 138.9 | C4—H, C4A—H, C5—H and C5A—H out of plane |
| 25 | 1104.8 | 192.4 | C8—H and C8A—H scissors |
| 26 | 1104.9 | 6.1 | C8—H and C8A—H scissors |
| 27 | 1189.6 | 7.2 | C8—H scissors |
| 28 | 1191.4 | 36.7 | C8—H scissors |
| 29 | 1193.8 | 14.5 | C8—H scissors |
| 30 | 1195.0 | 87.9 | C8—H scissors |
| 31 | 1238.7 | 215.4 | C—H scissors |
| 32 | 1309.3 | 8.5 | C—H scissors |
| 33 | 1325.1 | 10.0 | C—H scissors |
| 34 | 1367.8 | 29.0 | ring in plane |
| 35 | 1368.8 | 127.4 | ring in plane |
| 36 | 1386.4 | 1196.0 | 2,3 C—N symmetric stretch |
| 37 | 1386.8 | 171.6 | 2,3 C—N symmetric stretch |
| 38 | 1392.7 | 50.8 | C—H of the middle plane in plane bend;<br>C5—H in plane |
| 39 | 1394.9 | 545.0 | C—N symmetric stretch |
| 40 | 1395.5 | 51.6 | C—N symmetric stretch |
| 41 | 1399.3 | 85.7 | C5—H and C4—H in plane bend |
| 42 | 1413.9 | 111.8 | C—N stretch |
| 43 | 1414.8 | 69.7 | C—N stretch |
| 44 | 1483.0 | 127.1 | C═C bond bend |
| 45 | 1561.1 | 11.4 | middle benzene symmetric stretch |
| 46 | 1598.5 | 116.7 | —C—$NO_2$ $NO_2$ asymmetric stretch;<br>ring stretch of the benzene |
| 47 | 1601.1 | 73.6 | —C—$NO_2$ $NO_2$ asymmetric stretch;<br>ring stretch of the side benzene |
| 48 | 1649.9 | 35.8 | 1-$NO_2$ $NO_2$ asymmetric stretch |
| 49 | 1652.0 | 436.7 | 1,2,3-$NO_2$ $NO_2$ asymmetric stretch |
| 50 | 1653.9 | 121.0 | 3-$NO_2$ $NO_2$ asymmetric stretch |
| 51 | 1660.0 | 1178.1 | 1,3-$NO_2$ $NO_2$ asymmetric stretch |
| 52 | 1668.4 | 94.9 | 1,2,3-$NO_2$ $NO_2$ asymmetric stretch |
| 53 | 1671.1 | 178.4 | 1,2-$NO_2$ $NO_2$ asymmetric stretch |
| 54 | 1671.6 | 263.7 | 1,2-$NO_2$ $NO_2$ asymmetric stretch |
| 55 | 1689.1 | 25.3 | C═C stretch |
| 56 | 1689.8 | 85.7 | C═C stretch |
| 57 | 3173.2 | 10.3 | C═C stretch;<br>C4—H and C4A—H stretching |
| 58 | 3173.5 | 4.8 | C═C stretch;<br>C4—H and C4A—H stretching |
| 59 | 3189.6 | 13.4 | 1,2-C—H asymmetric stretch |
| 60 | 3204.8 | 11.4 | 1,2-C—H symmetric stretch |
| 61 | 3205.8 | 8.3 | 1,2-C—H symmetric stretch |
| 62 | 3244.2 | 8.2 | C5—H and C5A—H stretching |
| 63 | 3260.9 | 19.2 | C8—H stretching |
| 64 | 3260.9 | 16.2 | C8—H stretching |
| 65 | 3276.8 | 37.9 | C10—H stretching |

were assigned. The vibrational frequencies are identical on the whole between theoretical calculation and the experimental results. The predicted IR spectra using B3LYP/6-31G** level of theory and the experimental IR data for TNT-TTD are show in Fig. 3. Therefore the calculated data could provide the theoretical bases.

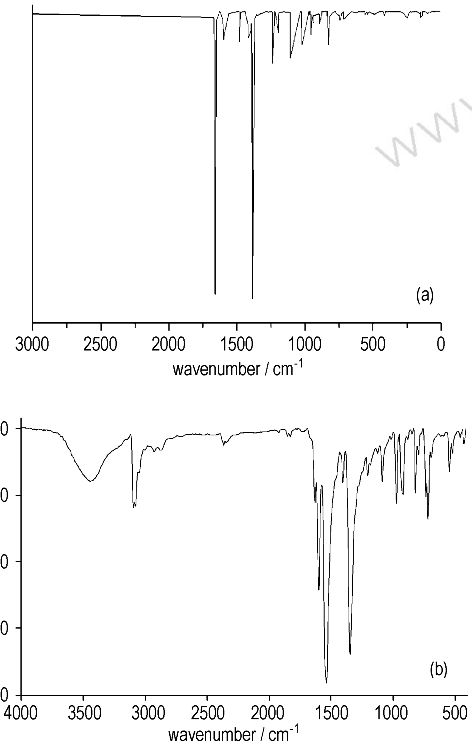


Fig. 3 The predicted IR spectra using B3LYP/6-31G* level of theory (a) and the experimental IR data (b) for TNT-TTD

### 3.3 Thermal behaviors

The DSC and TG-DTG curves of TNT-TTD are shown in Fig. 4 and Fig. 5, respectively. The FT-IR of the residual of the title compound at 400 ℃ is displayed in Fig. 6. It can be found that the nitro groups, C—H bonds disappear or diminish, that means the compound decomposed. There is one endothermic peak and a sequential exothermic peak appears at the 302 – 303 ℃ in the DSC curve. The decomposition process for the title compound begin at 311 ℃ and there is a largest mass loss rate 35.4% at 324 ℃ with a total mass loss of 18.3% during the range 311 ℃ to 375 ℃. After 375 ℃ the compound lose the mass at same rate until 516 ℃. There is a larger mass loss rate 17.5% at 617 ℃ with a total mass loss of 82.4% between 516 ℃ and 750 ℃. The compound decomposed completely after 750 ℃. The results show the TNT-TTD has high initial decomposed temperature and higher heat resistant ability. The melting point of TNT-TTD is 302 ℃ higher than TNT (80.9 ℃), 1,3,5-trinitrobenzen (TNB, 121.2 ℃), trinitro-m-xylene (TMX, 178 – 180 ℃) and trinitro-Mesitylene (TNTM, 229 ℃). Although the melting point of TNT-TTD is lower than HNS, it is a potential energetic material for its more positions than HNS that can be substituted by nitro-groups. So the higher nitrogenous content compounds to enhance the compounds' energy are expected to synthesize.

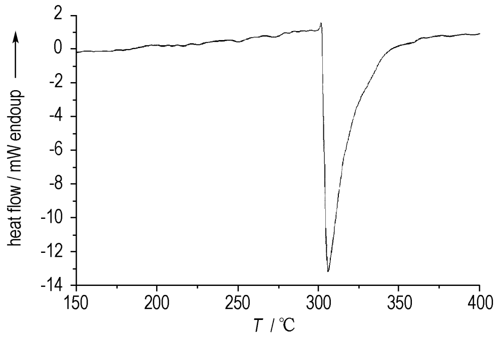


Fig. 4 The DSC curve of TNT-TTD

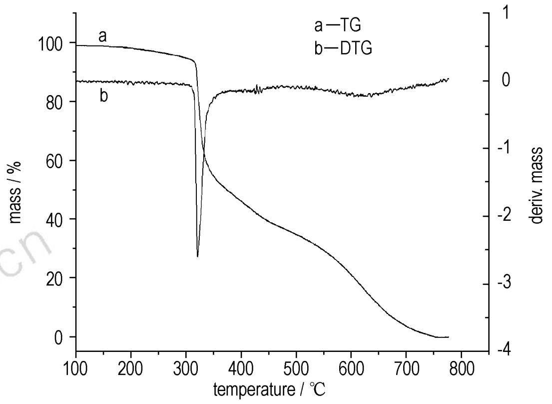


Fig. 5 TG-DTG curve of TNT-TTD

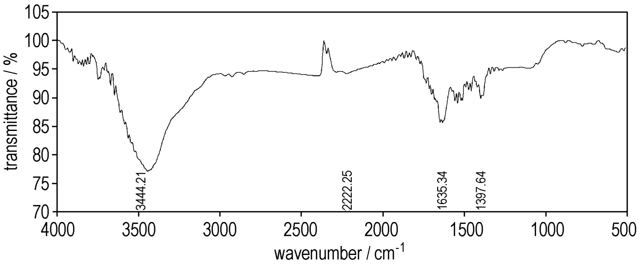


Fig. 6 The FT-IR of the residual of the TNT-TTD at 400 ℃

## 4 Conclusions

In summary, a new kind of stilbene has been prepared and its structure was characterized by $^1$H NMR, FT-IR and MS spectroscopy. The single-crystal X-ray analysis give evidence that its structure is similar to HNS, so it is expected to have the similar explosive properties. The thermal decomposition indicates that it has high thermal stability. Probably it can be used as heat resistant explosive and start materials for the new stilbene that has more nitro-groups substituent. It should be more reactivity than HNS owing to its more empty positions and be a potential organic intermediate and widely used in the industry. The DFT calculation results support the experimental geometrical data. The other properties and applications of the compound will be investigated in our future work.

**Supporting materials**: CCDC-268137 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www. ccdc. cam. ac. uk. /conts/retrieving. html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 122333603; e-mail: deposit@ ccdc. cam. ac. uk).

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# 1,4-对二(2,4,6-三硝基苯乙烯基)苯的合成、结构和性能

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**摘要**: 为了寻找新的多硝基芪耐热炸药,采用脑文格缩合反应制备得到了 1,4-对二(2,4,6-三硝基苯乙烯基)苯,并采用自然挥发溶剂法在 *N*,*N*-二甲基甲酰胺(DMF)溶液中培养了单晶。用 X-射线单晶衍射法测定了它的晶体结构,结果表明:该晶体属于三斜晶系,*P*-1 空间群,有一个对称中心。通过元素分析、FT-IR、$^1$H NMR、$^{13}$C NMR、MS 对化合物的结构作了进一步的表征,结果表明得到的化合物为目标化合物。采用 Gaussian 98 程序在 DFT-B3LYP/6-31G$^*$,6-311G$^{**}$水平下对化合物分子进行了几何优化和振动分析。计算结果无虚频,而且计算结果和试验结果一致,证明所得化合物结构相对稳定。通过差示扫描量热法(DSC)和热失重法(TG-DTG),在 10 ℃ · min$^{-1}$的升温速率下研究了化合物的热分解性能,此化合物有较高的熔点(302 ℃)和热分解温度(311 ℃),结果表明该化合物有较高的耐热性能。

**关键词**: 有机化学; 多硝基多芪类化合物; 分子结构; 密度泛函理论; 热分解性能

**中图分类号**: TJ55; O62　　**文献标识码**: A