

Theoretical studies on vibrational spectra, thermodynamic properties, detonation properties and pyrolysis mechanism for 1,2-bis(2,4,6-trinitrophenyl) hydrazine

Li Xiao-Hong · Zhang Rui-Zhou · Zhang Xian-Zhou

Received: 12 September 2011 / Accepted: 4 November 2011 / Published online: 30 November 2011
© Springer-Verlag 2011

Abstract The thermal stability and pyrolysis mechanism of 1,2-bis(2,4,6-trinitrophenyl) hydrazine were investigated based on fully optimized molecular geometric structures. The results demonstrate the existence of intramolecular hydrogen bond interactions 1,2-bis(2,4,6-trinitrophenyl) hydrazine. The assigned infrared spectrum was also obtained; the results reveal four main characteristic regions in the calculated IR spectra of the title compound. Detonation velocities (D) and pressures (P) were also evaluated by using Kamlet-Jacobs equations based on the calculated density and heat of formation. Thermal stability and the pyrolysis mechanism of 1,2-bis(2,4,6-trinitrophenyl) hydrazine were investigated by calculating the bond dissociation energies at the B3LYP/6–31 G* level.

Keywords 1,2-Bis(2,4,6-trinitrophenyl) hydrazine · Pyrolysis mechanism · Detonation properties · Infrared spectrum

Introduction

Energetic materials (explosives, propellants and pyrotechnics) are used extensively for both civil and military

applications. The nitro alkyl and aryl derivatives of hydrazine possess good high-energy properties and are used as explosives and rocket propellants. Research has shown that hydrazine and its alkylated derivatives burn rapidly and completely in air with considerable evolution of heat [1]. It is reported that the thermal stability of a molecule can be improved by the introduction of an amino group into an aromatic ring, condensation of picryl chloride into an appropriate moiety, or through the introduction of conjugation [2]. By determining various explosive parameters [3] such as oxygen balance, velocity of detonation [4], density and heat of formation, we can evaluate the explosive performance [5] of synthesized compounds. Exploring microscopic pyrolysis mechanisms, i.e., addressing the question of how an important impulse can initiate rapid exothermic reactions leading to the detonation of explosive solids, remains a key research target for both theoretical and experimental chemists.

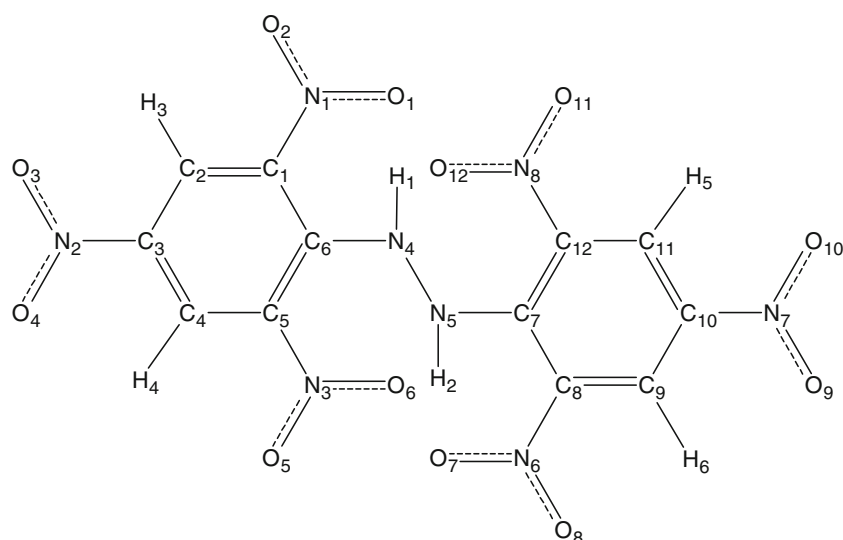
In general, initiation of detonation involves the complex interplay of molecular, crystalline and physical factors [6–8]. Kamlet and Adolph suggested that correlations with a single factor can indeed exist if others are kept as uniform as possible [6, 7]. However, Brill and James [8] pointed out that a correlation does not necessarily imply a causal relationship; it may simply be symptomatic.

The nitro alkyl and aryl derivatives of hydrazine have been reported to possess good high-energy features such as explosive and rocket propellant properties. Hydrazine and its alkylated derivatives burn rapidly and completely in air with considerable evolution of heat [1]. Badgular et al. [9] stated that 1,2-bis(2,4,6-trinitrophenyl) hydrazine (see Fig. 1) is one of the precursors in the synthesis of the important energetic material hexanitrazobenzene. Recently, 1,2-bis(2,4,6-tri-

L. Xiao-Hong (✉) · Z. Rui-Zhou
College of Physics and Engineering,
Henan University of Science and Technology,
Luoyang 471003, China
e-mail: lorna639@126.com

Z. Xian-Zhou
College of Physics and Information Engineering,
Henan Normal University,
Xinxiang 453007, China

Fig. 1 Molecular structure and atomic numbering of 1,2-bis(2,4,6-trinitrophenyl) hydrazine



trinitrophenyl) hydrazine was synthesized by the condensation of picryl chloride with hydrazine hydrate [10]. To date, no theoretical investigations on its structure and properties can be found in the literature. Since studies on structure–performance relationships are the basis of molecular design, in this paper, the title compound was fully optimized at the DFT-B3LYP/6–31 G* level to obtain its molecular geometry and electronic structure. Spectra were obtained and assigned by vibrational analysis. In addition, the thermal stability and sensitivity were studied, and density and detonation properties predicted. This work aims to lay a good foundation for studying and further exploiting the structures and properties of 1,2-bis(2,4,6-trinitrophenyl) hydrazine.

Computational methods

The DFT-B3LYP method [10, 11] in combination with the 6-31G* [12] basis set has been used widely in many investigations [13–15], and can yield reasonable energies, molecular structures, and infrared vibrational frequencies. In this paper, 1,2-bis(2,4,6-trinitrophenyl) hydrazine was fully optimized to obtain its molecular geometry and electronic structure. Vibrational analysis was then performed at the same level with the Gaussian03 program package [16]. Since DFT-calculated harmonic vibrational frequencies are usually larger than those observed experimentally, they were scaled using a factor of 0.96 as has been done before [17].

Furthermore, the theoretical vibrational spectra of the title compound were interpreted by means of potential energy distribution (PED) with version V7.0-G77 of the MOLVIB program written by Sundius [18, 19]. The calculated Raman activity (S_i) was converted to relative

intensity (I_i) using the following relationship derived from the basis theory of Raman scattering [20, 21]:

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[1 - \exp\left(\frac{-hc v_i}{kT}\right) \right]} \quad (1)$$

Where v_0 is the exciting frequency (in cm^{-1} units), v_i is the vibrational wavenumber of the i th normal mode, h , c and k are universal constants, and f is the suitably chosen common scaling factor for all peak intensities.

Detonation velocity (D) and pressure (P) are the most important targets used to scale the detonation characteristics of energetic materials. Kamlet-Jacobs (K-J) equations [22, 23] are used to calculate D and P to quantitatively evaluate high energy density compounds in molecular design. For explosives with CHNO elements, these parameters can be calculated using the following K-J equations:

$$D = 0.7062 \times \Phi^{0.5} (1.0 + 1.3\rho) \quad (2)$$

$$\Phi = N \bar{M}^{0.5} Q^{0.5}$$

$$P = 7.617 \times 10^8 \Phi \rho^2 \quad (3)$$

where terms in Eqs. 2 and 3 are defined as follows: P , detonation pressure (GPa); D , detonation velocity (km/s); ρ , packed density (g/cm^3); Φ , characteristic value of explosive; N , moles of gas produced by per gram of explosive; \bar{M} , average molar weight of detonation products; and Q , estimated heat of detonation (KJ/g). The density is obtained according to [24], in which the electrostatic potential is considered.

Table 1 Geometric parameters of 1,2-bis(2,4,6-trinitrophenyl)hydrazine at the B3LYP/6-31 G* level

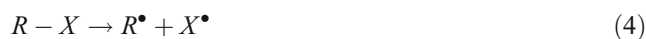
Bond length(Å)		Bond angle(°)		Dihedral angle(°)	
C1-N1	1.466	N2-C3-C2	119.53	O1-N1-C1-C2	178.66
C3-N2	1.467	N2-C3-C4	119.47	O2-N1-C1-C2	-0.56
C5-N3	1.471	C2-C3-C4	120.98	O1-N1-C1-C6	-2.96
C6-N4	1.360	N3-C5-C4	115.10	O2-N1-C1-C6	177.81
C1-C2	1.390	N3-C5-C6	122.0	C1-C2-C3-C4	2.91
C2-C3	1.384	C4-C5-C6	122.57	C2-C3-C4-C5	-0.73
C3-C4	1.390	N1-C1-C2	115.67	C3-C4-C5-C6	-4.81
C4-C5	1.384	N1-C1-C6	122.38	C4-C5-C6-C1	7.61
C5-C6	1.425	C2-C1-C6	121.93	C4-C5-C6-N4	-170.89
C6-C1	1.434	C1-C2-C3	119.63	C5-C6-N4-N5	16.29
N4-N5	1.383	C3-C4-C5	119.28	C1-C6-N4-N5	-162.13
N5-C7	1.370	C1-C6-C5	115.19	C6-N4-N5-C7	125.17
N6-C8	1.469	C1-C6-N4	120.74	N4-N5-C7-C8	145.33
N7-C10	1.468	C5-C6-N4	124.05	N4-N5-C7-C12	-33.05
N8-C12	1.475	C6-N4-N5	124.64	N5-C7-C8-C9	-175.78
C7-C8	1.431	N4-N5-C7	119.57	N5-C7-C12-C11	173.64
C8-C9	1.391	N5-C7-C8	122.23	N5-C7-C12-N8	-11.85
C9-C10	1.384	N5-C7-C12	122.90	C7-C8-C9-C10	0.41
C10-C11	1.391	C8-C7-C12	114.85	C8-C9-C10-C11	-1.74
C11-C12	1.383	N8-C12-C7	121.32	C9-C10-C11-C12	-0.26
C12-C7	1.424	N8-C12-C11	115.20	C10-C11-C12-C7	3.75
N1-O1	1.222	C7-C12-C11	123.27	O3-N2-C3-C2	0.22
N1-O2	1.245	N6-C8-C7	122.25	O3-N2-C3-C4	178.52
N2-O3	1.229	N6-C8-C9	115.61	O4-N2-C3-C2	-179.83
N2-O4	1.229	C7-C8-C9	122.12	O4-N2-C3-C4	-1.53
N3-O5	1.224	N7-C10-C9	119.62	C1-C6-N4-H1	9.21
N3-O6	1.235	N7-C10-C11	119.11	C5-C6-N4-H1	-172.37
N6-O7	1.224	C9-C10-C11	120.96	H1-N4-N5-H2	101.93
N6-O8	1.239	C10-C11-C12	118.92	H1-N4-N5-C7	-45.92
N7-O9	1.228	C8-C9-C10	119.71	O5-N3-C5-C4	39.59
N7-O10	1.229	C1-N1-O1	118.16	O5-N3-C5-C6	-146.88
N8-O11	1.226	C1-N1-O2	118.72	O6-N3-C5-C4	-135.30
N8-O12	1.230	C3-N2-O3	117.31	O6-N3-C5-C6	38.24
H1-N4	1.020	C3-N2-O4	117.14		
H2-N5	1.021	C8-N6-O7	118.31		
		C8-N6-O8	117.87		
		C10-N7-O9	117.30		
		C10-N7-O10	117.06		

As a high energy explosive, the thermal stability of the title compound is important. The bond dissociation energies

Table 2 Selected hydrogen bond lengths (Å) and bond angles (°) calculated using the B3LYP/6-31 G* method

D-H...A	d(D-H)	D(H...A)	D(D...A)	∠DHA
N ₄ -H ₁ ...O ₁	1.020	1.791	2.595	130.07
N ₅ -H ₂ ...O ₇	1.021	1.847	2.623	132.77

(BDEs) of various bonds in the molecule can be calculated to measure the strength of bonds and relative stabilities of the title compound. BDE is the energy required in homolysis of a bond and is denoted commonly by the difference between the total energies of the product and the reactant. The homolysis and BDE of the R-X bond are shown as follows:



$$BDE_{R-X} = E(R^{\bullet}) + E(X^{\bullet}) - E(R-X) \quad (5)$$

Table 3 Calculated (B3LYP method) and experimental fundamental frequencies (cm^{-1}) for the title compound. First numbers in parentheses in column 2 correspond to IR intensities and the second to Raman intensities. α Planar ring deformation, Φ non-planar ring deformation, ν stretching, δ bending, ip in-plane deformation, oop out-of-plane deformation, ν_{ss} symmetric stretching, ν_{ass} asymmetric stretching, ω wagging, ϕ scissoring, PED potential energy distribution

	Calculated frequencies	Experimental ^a (IR)	Assignments[PED]
1	394(15.55,0.68)		$\Phi(\text{ring})$ [82]
2	416(8.52,0.78)		$\Phi(\text{ring})$ [85]
3	429(10.23,1.83)		$\delta(\text{CNN})$ [62],
4	464(2.41,1.08)		$\Phi(\text{ring})$ [90]
5	504(0.93,6.41)		$\Phi(\text{ring})$ [87]
6	508(1.07,2.42)		$\Phi(\text{ring})$ [81]
7	524(2.88,3.52)		$\Phi(\text{ring})$ [80]
8	525(8.04,39.58)		$\delta(\text{N-H})$ [57], $\Phi(\text{ring})$ [33]
9	542(11.93,23.44)		$\delta(\text{N-H})$ [57], $\Phi(\text{ring})$ [33]
10	547(61.47,148.58)		$\delta(\text{N-H})$ [72]
11	570(6.39,0.59)		$\tau(\text{CCNO})$ [75]
12	635(73.95,14.96)		$\Phi(\text{ring})$ [57], $\delta(\text{N-H})$ [31]
13	647(12.01,6.02)		ωNO_2 [45], $\Phi(\text{ring})$ [41]
14	669(4.72,92.40)		$\delta(\text{N-H})$ [62]
15	675(30.76,122.16)		$\alpha(\text{ring})$ [37], $\delta(\text{N-H})$ [54]
16	699(8.62,2.16)		$\Phi(\text{ring})$ [81]
17	701(59.65,27.20)		$\alpha(\text{ring})$ [85]
18	702(57.53,2.54)		ωNO_2 [82]
19	710(68.52,34.90)		ωNO_2 [42], $\Phi(\text{ring})$ [44]
20	712(37.03,13.56)		ωNO_2 [45], $\Phi(\text{ring})$ [41]
21	718(77.99,89.24)		ωNO_2 [57], $\delta(\text{N-H})$ [32]
22	727(18.12,23.74)		$\Phi(\text{ring})$ [40], ωNO_2 [52]
23	734(4.34,5.19)		$\Phi(\text{ring})$ [50], ωNO_2 [42]
24	736(8.25,6.27)		$\Phi(\text{ring})$ [54], ωNO_2 [41]
25	749(18.20,77.96)		$\Phi(\text{ring})$ [62]
26	761(1.90,30.21)		$\alpha(\text{ring})$ [45], ϕNO_2 [47]
27	803(10.91,6.64)		$\alpha(\text{ring})$ [48], ϕNO_2 [38]
28	804(9.44,1.73)		$\alpha(\text{ring})$ [85]
29	807(11.58,112.09)		$\delta(\text{CNN})$ [74]
30	910(30.31,12.97)		$\nu(\text{C-N})$ [78]
31	911(90.56,19.37)		$\nu(\text{C-N})$ [75]
32	920(41.59,20.50)		$\delta(\text{C-H})_{oop}$ [42], $\nu(\text{C-N})$ [32]
33	922(6.46,20.28)		$\delta(\text{C-H})_{oop}$ [40], $\nu(\text{C-N})$ [31]
34	928(12.07,9.34)		$\delta(\text{C-H})_{oop}$ [95]
35	932(8.39,2.25)		$\delta(\text{C-H})_{oop}$ [93]
36	940(7.46,2.62)		$\delta(\text{C-H})_{oop}$ [95]
37	941(4.40,2.24)		$\delta(\text{C-H})_{oop}$ [95]
38	1,062(38.12,19.85)		$\delta(\text{C-H})_{ip}$ [92]
39	1,064(105.48,5.91)		$\delta(\text{C-H})_{ip}$ [95]
40	1,115(17.80,14.50)		$\delta(\text{C-H})_{ip}$ [57], $\nu(\text{N-N})$ [35]
41	1,146(136.16,27.86)		$\alpha(\text{ring})$ [89]
42	1,151(3.60,153.75)		$\alpha(\text{ring})$ [87]
43	1,154(24.69,3.58)		$\delta(\text{C-H})_{ip}$ [90]

Table 3 (continued)

	Calculated frequencies	Experimental ^a (IR)	Assignments[PED]
44	1,186(8.44,4.90)		$\delta(\text{C-H})_{ip}$ [61], $\nu(\text{N-N})$ [32]
45	1,246(62.28,58.76)		$\delta(\text{C-H})_{ip}$ [71]
46	1,271 (57.90,154.51)		$\nu(\text{C-N})$ [47], $\delta(\text{N-H})$ [42]
47	1,298(320.91,33.21)		$\nu(\text{C=C})_{Ph}$ [78]
48	1,302(107.64,68.05)		$\nu(\text{C=C})_{Ph}$ [72]
49	1,317(166.22,69.86)		$\nu(\text{C-N})$ [61]
50	1,333 (525.84,224.24)		$\nu_{ss}(\text{NO}_2)$ [81]
51	1,334 (704.57,325.35)		$\nu_{ss}(\text{NO}_2)$ [74]
52	1,340(1.25,304.26)		$\nu(\text{C=C})_{Ph}$ [62]
53	1,346 (107.39,331.82)		$\nu_{ss}(\text{NO}_2)$ [87]
54	1,351(96.08,250.96)	1,350	$\nu_{ss}(\text{NO}_2)$ [85]
55	1,386(2.41,18.80)		$\nu(\text{C=C})_{Ph}$ [72]
56	1,388 (0.81,38.90)		$\nu(\text{C=C})_{Ph}$ [70]
57	1,423(58.50,5.21)		$\nu(\text{C=C})_{Ph}$ [50], $\delta(\text{N-H})$ [40]
58	1,436(81.26,12.53)		$\nu(\text{C=C})_{Ph}$ [50], $\delta(\text{N-H})$ [38]
59	1,571 (321.04,102.98)		$\nu(\text{C=C})_{Ph}$ [55], $\nu(\text{N-C})$ [25]
60	1,507 (208.60,186.59)		$\nu(\text{C=C})_{Ph}$ [54], $\nu(\text{N-C})$ [32]
61	1,544(31.78,49.87)		$\nu(\text{C=C})_{Ph}$ [85]
62	1,546(10.91,31.04)		$\nu(\text{C=C})_{Ph}$ [82]
63	1,560(14.21,233.84)		$\nu(\text{C=C})_{Ph}$ [55], $\nu_{ass}(\text{NO}_2)$ [38]
64	1,572(95.23,76.63)		$\nu(\text{C=C})_{Ph}$ [65]
65	1,582(107.81,7.46)		$\nu_{ass}(\text{NO}_2)$ [60], $\delta(\text{N-H})$ [31]
66	1,588(16.39,16.95)		$\nu_{ass}(\text{NO}_2)$ [54], $\delta(\text{N-H})$ [41]
67	1,605(610.26,13.06)		$\nu_{ass}(\text{NO}_2)$ [74]
68	1,606(250.80,11.11)		$\nu_{ass}(\text{NO}_2)$ [70]
69	1,609(532.35,37.25)	1,600	$\nu(\text{C=C})_{Ph}$ [60], $\nu_{ass}(\text{NO}_2)$ [31]
70	1,619(86.34,90.41)		$\nu(\text{C=C})_{Ph}$ [61], $\nu_{ass}(\text{NO}_2)$ [31]
71	3,136 (18.44,38.97)		$\nu(\text{C-H})_{Ph}$ [98]
72	3,139(21.79,48.70)		$\nu(\text{C-H})_{Ph}$ [98]
73	3,147(35.91,45.66)		$\nu(\text{C-H})_{Ph}$ [98]
74	3,148(28.23,45.20)	3,030	$\nu(\text{C-H})_{Ph}$ [98]
75	3,310 (149.22,515.67)		$\nu(\text{N-H})$ [100]
76	3,319 (147.89,494.45)		$\nu(\text{N-H})$ [100]

^a Data from [9]

While calculating BDE values, zero point vibrational energy (ZPVE) corrected energies had to be used and basis set superposition error (BSSE) calculations were required.

Results and discussion

Molecular structure

Table 1 lists the fully optimized geometric parameters of the title compound, such as bond lengths, bond angles and dihedral angles. To the best of our knowledge, experimental data on the geometric structure of the title compound are not available in the literature.

From Table 1, it can be seen that the bond length of N₄–N₅ equal to 1.383 Å is smaller than the usual N–N single bond (1.45 Å) and the N–N bond length of hydrazine (also 1.45 Å). The bond lengths of C₅–N₃ and C₁₂–N₈ are 1.471 and 1.475 Å, respectively, i.e., longer than the normal C–N single bond length (1.47 Å) [25], while the bond lengths of C₁–N₁, C₃–N₂, C₈–N₆ and C₁₀–N₇ are between 1.466 and 1.469 Å, which is smaller than that of the single (C–N, 1.47 Å) bond length. In addition, the bond lengths of C₆–N₄ and C₇–N₅ are 1.360 and 1.370 Å, respectively. These variations in bond lengths are due mainly to the electronic delocalization in the molecule.

Interestingly, geometry optimization performed on the title compound indicated that it exhibits intramolecular hydrogen bond interaction. The hydrogen bond lengths and angles are listed in Table 2.

From the data on dihedral angles in Table 1, we can see that the dihedral angle of C₆–C₅–N₃–O₆ is 38.24°, while the dihedral angles of C₆–C₁–N₁–O₁, C₄–C₃–N₂–O₃ are –2.96° and 178.52°, respectively, which shows that the nitro group (on C₅) linked with phenyl leaves the benzene plane because of the steric hindrance effect, and the other two nitro groups (on C₁ and C₃) are co-planar with

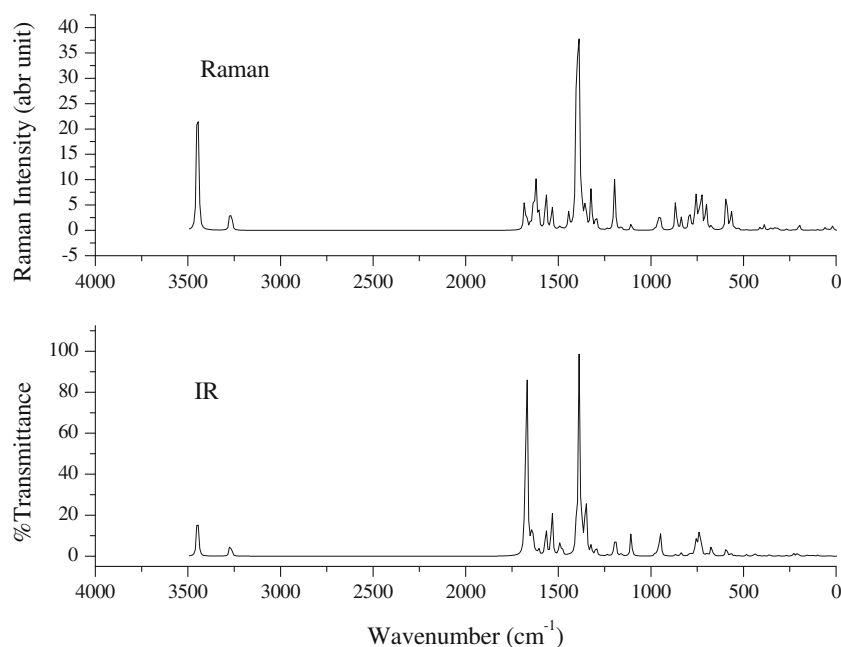
benzene. Thus, we can explain why the bond length of the C₅–N₃ bond (i.e., 1.471 Å) is larger than those of C₁–N₁ (1.466 Å) and C₃–N₂ (1.467 Å), and why the former has smaller bond populations (0.22856e for C₅–N₃) than the latter (0.24633e for C₃–N₂, 0.23232e for C₁–N₁), which indicates that the C₅–N₃ bond is relatively weaker than the C₁–N₁ and C₃–N₂ bonds.

Infrared- and raman-spectra

As is well known, the IR spectrum is one basic property of a compound, and is also an effective measure with which to analyze or identify substances. It also has a direct relationship with the molecule's thermodynamic properties. However, for some reason, little experimental data [10] are available on the IR spectra and thermodynamic properties of 1,2-bis(2,4,6-trinitrophenyl) hydrazine. Therefore, it is of great of significance to calculate the IR and thermodynamic properties of 1,2-bis(2,4,6-trinitrophenyl) hydrazine by theoretical methods. Here, vibrational frequencies were calculated using DFT at the B3LYP/6-31 G* level. Table 3 presents the calculated vibrational frequencies, IR intensities and Raman activity of the title compound. Figure 2 provides its IR and Raman spectra.

From Table 3 and Fig. 2, four main characteristic regions can be identified. In the 3136–3148 cm⁻¹ range, the modes are associated with the C–H stretching vibrations, and, in this region, the number of vibration equals that of C–H bonds. For instance, the title compound has four bands of 3136, 3139, 3147, 3148 cm⁻¹. The strong characteristic peaks in the 1560–1619 cm⁻¹ range corre-

Fig. 2 Calculated FT-IR and FT-Raman spectra of the title compound at the B3LYP/6-31 G* level



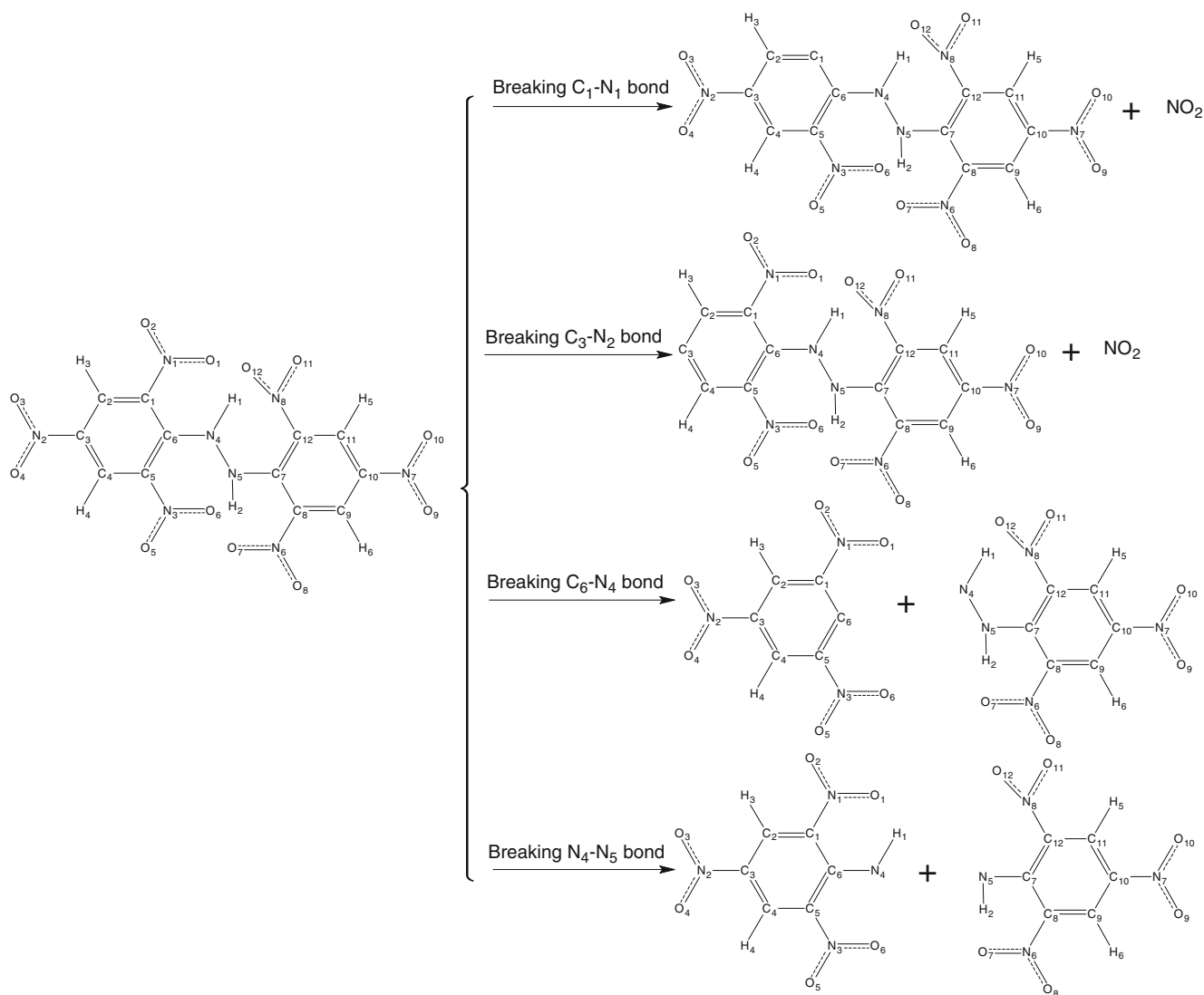


Fig. 3 The homolysis process and the radical species from related homolysis

spond to the N=O asymmetric stretching motion of nitro groups. Another remarkable signal centering at 1333–1351 cm^{-1} is associated with the N=O symmetric stretch of nitro groups. Finally, the weak peaks at less than 1300 cm^{-1} are caused mainly by the C–NO₂ stretch, C–H bending vibration and the deformation of the phenyl skeleton, which is located in the fingerprint region and can be used to identify isomers.

To testify the reliability of theoretical computation, some of experimental vibrational frequencies [9] are also listed in Table 3 and compared with theoretical calculations. In addition, experimental [9] data show that the strong characteristic peaks in the 3400–3200 cm^{-1} range correspond to the N–H stretching vibration. From the limited frequencies available from experimental data, it is noted that the calculated frequencies at the B3LYP/6–31 G* level

Table 4 Total energies (Hartree) and bond dissociation energies (BDE; kJ mol^{-1}) for the title compound and related radical species

Breaking bonds	Reactant total energy	Zero point energy	Product energy 1	Product energy 2	BDE ^a
C ₁ -N ₁	-1,800.7026	0.2293	-1,595.5513	-205.0634	230.76
C ₃ -N ₂	-1,800.7026	0.2293	-1,595.5339	-205.0634	276.42
C ₆ -N ₄	-1,800.7026	0.2293	-955.6342	-844.9447	324.66
N ₄ -N ₅	-1,800.7026	0.2293	-900.3127	-900.3127	202.60

^a BDE corrected by zero-point energies (ZPE) and basis set superposition error (BSSE)

Table 5 Predicted density and detonation properties of the title compound. *OB* Oxygen balance. *HOF* heat of formation

Compound	Condensed HOF (kJ mol ⁻¹)	OB ₁₀₀	V (cm ³ mol ⁻¹)	ρ (g cm ⁻³)	Q (J g ⁻¹)	D (km s ⁻¹)	P (GPa)	H ₅₀ (cm)
1,2-bis(2,4,6-trinitrophenyl) hydrazine	252.58	-0.528	262.43	1.73	6,055	7.59(7.92 ^b)	24.95	90 ^b
RDX ^a	–	-0.216	–	1.81	–	8.75	34.7	16
HMX ^a	–	-0.216	–	1.90	–	9.10	39.0	19

^a Data for RDX and HMX are from [25]

^b Data from [9]

are close to the experimental values, which proves the reliability of the computed IR spectrum. The trivial discrepancy is perhaps due to the intermolecular interactions existing in experimental samples. Another reason could be that the theoretical computation aims at the isolated “gas” molecule and is based on the simple harmonic mode.

Pyrolysis mechanism

Another main concern regarding energetic materials is whether they are kinetically stable enough to be of practical interest. Thus, studies on the bond dissociation or pyrolysis mechanism are important, and are essential to understanding the decomposition process of energetic materials because they concern directly the sensitivity and stability of energetic compounds. In this paper, four possible initial steps in the pyrolysis route are considered by breaking the following bonds: (1) C₁–N₁; (2) C₃–N₂; (3) C₆–N₄; (4) N₄–N₅. Figure 3 presents the stable structures of the title compound and the radical species from the related homolysis, and Table 4 lists the total energies, BDEs of the title compound and the related radical species for the homolysis of the bonds.

Generally speaking, the less energy required to break a bond, the weaker the bond is, and the more easily that bond becomes a trigger bond. From Table 4, it can be noted that the BDE of homolysis of the N₄–N₅ bond is 202.60 kJ mol⁻¹, which is the least among the four possible initial steps, suggesting that the

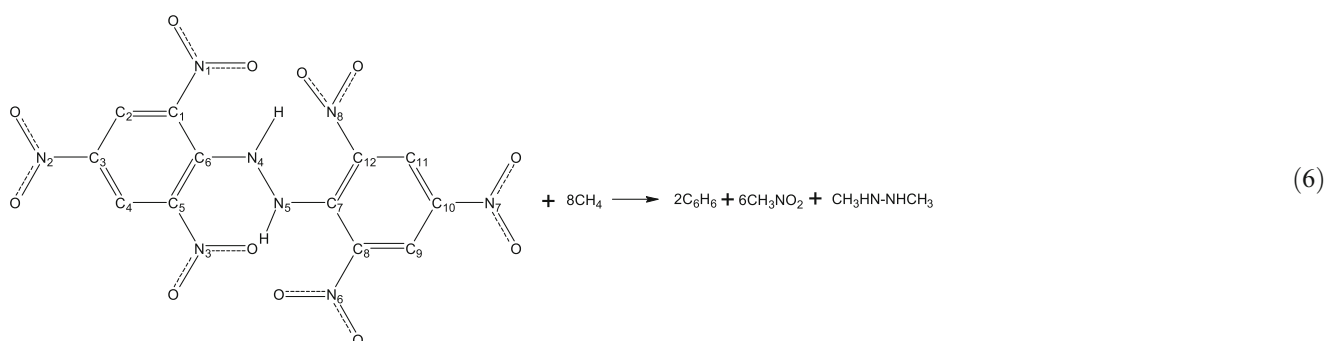
N₄–N₅ bond may be a trigger bond during the thermolysis initiation process. In addition, it is also noted that the BDE of the homolysis of the C₁–N₁ bond is 230.76 kJ mol⁻¹, which is close to that of the N₄–N₅ bond. The BDEs of the homolysis of the C₃–N₂ and C₆–C₄ bonds are 276.42 and 324.66 kJ mol⁻¹, respectively, which is much bigger than that of the N₄–N₅ bond. Through comparing the BDEs of C₁–N₁, C₃–N₂ and C₆–C₄ bonds with that of the N₄–N₅ bond, we think that the N₄–N₅ bond may be a trigger bond.

Detonation properties

Detonation velocity (D) and pressure (P) are important parameters in evaluating the performances of energetic materials. With C-, H-, O-, and N-containing explosives, they can be estimated using K-J equations [22, 23].

One can use the atomization reaction or isodesmic reaction method to obtain the standard heats of formation (HOF) at 298.15 K. In this paper, the isodesmic reaction method was employed. The isodesmic reaction, where the numbers of bonds and bond types are preserved on both sides of the reaction, often leads to cancellation of systematic errors resulting from bond environments, spin contamination, basis set superposition and other nonrandom factors [26]. The accuracy of HOF obtained theoretically is conditioned by the reliability of HOF of the reference compounds.

The HOF for the title compound can be derived from the following isodesmic reaction (Eq. 6):



Where the experimental HOFs for CH₄, C₆H₆, CH₃NO₂ and CH₃HN–NHCH₃ are –17.9 kcal mol^{–1} [27], 16.2 kcal mol^{–1} [28], –19.3 kcal mol^{–1} [27] and 22.22 kcal mol^{–1} [29], respectively. Further, we computed the condensed phase HOF of the title compound through the method of Byrd and Rice [30]. Table 5 lists the calculated condensed HOF, V, ρ, D, P, Q and the oxygen balances (OB₁₀₀) of the title compound. The OB₁₀₀ are calculated using Eq. 7, which can be used to roughly predict the impact sensitivities of the explosives [31].

$$OB_{100} = \frac{n_O - (0.5 \cdot n_H + 2n_C)}{M} \times 16 \quad (7)$$

Where n_O, n_H and n_C represent the numbers of O, H and C atoms, respectively; M is the molecular weight.

Experimental data [32] for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are also listed in Table 5. The impact sensitivity H₅₀ of the title compound, as well as RDX and HMX are also included in Table 5. It is noted that 1,2-bis(2,4,6-trinitrophenyl) hydrazine is impact insensitive to 90 cm, which suggests that it has low vulnerability to mechanical stimuli compared to that of other nitramine explosives such as RDX and HMX.

It is noted that values of D and P for 1,2-bis(2,4,6-trinitrophenyl) hydrazine are 7.59 km/s and 24.95 GPa, respectively. The values of ρ, D, P of the title compound are smaller than those of RDX and HMX, i.e., the values of ρ, D, P of the title compound do not satisfy the quantitative standard of a high energetic density compound (HEDC) (ρ≈1.9 g/cm³, D≈9.0 km/s, P=40 GPa) [33], although the thermal stability of the title compound is good and the values of ρ, D, P are relatively high. Based on our previous works [13, 14], 1,2-bis(2,4,6-trinitrophenyl) hydrazine can become a HEDC by adding more –NO₂ groups to improve ρ, D, P.

Conclusions

Using DFT B3LYP/6-31 G*, we studied the molecular structure and thermochemistry properties of the title compound. The obtained conclusions are as follows:

- (1) Geometry optimization performed on the title compound indicated that it exhibits intramolecular hydrogen bond interaction.
- (2) There are four main characteristic regions in the calculated IR spectrum of the title compound. In the 3136–3148 cm^{–1} range, the modes are associated with C–H stretching vibrations. The strong characteristic peaks in the 1560–1619 cm^{–1} range correspond to the N=O asymmetric stretch of nitro groups. Another

remarkable signal centering at 1333–1351 cm^{–1} is associated with N=O symmetric stretch of nitro groups. Finally, the weak peaks at less than 1300 cm^{–1} are caused mainly by the C–NO₂ stretch, C–H bending vibration, and deformation of the phenyl skeleton.

- (3) The N₄–N₅ and C₁–N₁ bonds of the title compound may possibly be trigger bonds.

Acknowledgments We gratefully thank the National Natural Science Foundation of China (Grant 10774039), the grant from Development Program in Science and Technology of Henan Province (No. 102300410114 and No. 112300410206), Henan University of Science and Technology for Young Scholars (No. 2009QN0032) for their support of this work.

References

1. Puri K (1995) Textbook of principles of inorganic chemistry, 5th edn. Chand, Delhi, 1995
2. Agrawal JP, Prasad US, Survey RN (2000) Synthesis of 1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene and its thermal and explosive behavior. *New J Chem* 24:583–585
3. Keshavarz MH (2009) Novel methods for predicting densities of polynitro arene and polynitro hetero arene explosive in order to evaluate their detonation performance. *J Hazard Mater* 165:579–588
4. Schubert H (1996) Explosivstoffe für militärische Anwendungen. *Spektrum Wiss* 8:97–101
5. Sikder AK, Maddala G, Agrawal JP, Singh H (2001) Important aspects of behavior of organic energetic compounds: a review. *J Hazard Mater* 84:1–26
6. Kamlet MJ (1976) In: Proceedings of the 6th Symposium (International) Deton. Report No ACR 221:312
7. Kamlet MJ, Adolph HG (1979) The relationship of impact sensitivity with structure of organic high explosives. *Propell Expl* 4:30–34
8. Brill T, James K (1993) Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives. *Chem Rev* 93:2667–2692
9. Badgujara DM, Talawar MB, Harlapur SF, Asthana SN, Mahuliker PP (2009) Synthesis, characterization and evaluation of 1,2-bis(2,4,6-trinitrophenyl) hydrazine: a key precursor for the synthesis of high performance energetic materials. *J Hazard Mater* 172:276–279
10. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
11. Becke D (1992) Density-functional thermochemistry. 2. The effect of the Perdew-Wang generalized-gradient correlation correction. *J Chem Phys* 97:9173–9177
12. Hariharan PC, Pople JA (1973) The influence of polarization functions on molecular orbital hydrogenation energies. *Theor Chim Acta* 28:213–222
13. Li XH, Zhang RZ, Zhang XZ (2010) Computational study of imidazole derivative as high energetic materials. *J Hazard Mater* 183:622–631
14. Li XH, Cheng QD, Zhang XZ (2010) Density functional theory study of several nitrotriazole derivatives. *J Energ Mater* 28:251–272
15. Xu XJ, Xiao HM, Ju XH, Gong XD, Zhu WH (2006) Theoretical studies on heats of formation for polynitrocubanes using the

- density-functional theory B3LYP method and semi empirical MO. *J Phys Chem A* 110:5929–5933
16. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JAJ, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJK, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (2003) Gaussian Inc, Pittsburgh PA
 17. Scott P, Radom L (1996) Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Moeller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *J Phys Chem* 100:16502–16513
 18. Sundius T (2002) MOLVIB: a program for harmonic force field calculations, QCPE program No. 807
 19. Sundius T (2002) Scaling of ab initio force fields by MOLVIB. *Vib Spectrosc* 29:89–95
 20. Keresztury G, Holly S, Varga J, Besenyi G, Wang AY, Durig JR (1993) Vibrational spectra of monothiocarbamates. II. IR and Raman spectra, structure, and ab initio force field of S-methyl-N, N-dimethylthiocarbamate. *Spectrochim Acta A* 49:2007–2026
 21. Keresztury G, Chalmers JM, Griffith PR (2002) Raman spectroscopy: theory in handbook of vibrational spectroscopy, vol 1. Wiley, New York
 22. Kamlet MJ, Jacobs SJ (1968) Chemistry of detonation. I. A simple method for calculating detonation properties of C-H-N-O explosives. *J Chem Phys* 48:23–35
 23. Zhang XH, Yun ZH (1989) Explosive chemistry. National Defence Industry Press, Beijing, People's Republic of China
 24. Politzer P, Martinez J, Jane Murray S, Monica Concha C, Alejandro T (2009) An electrostatic interaction correction for improved crystal density prediction. *Mol Phys* 107:2095–2101
 25. Sasada Y (1984) Molecular and crystal structures in chemistry handbook, 3rd edn. The Chemical Society of Japan, Maruzen, Tokyo
 26. Hehre WJ, Radom L, Pvr S (1986) Ab initio molecular orbital theory. Wiley, New York
 27. Rice BM, Sahu S, Owens FJ (2002) *J Mol Struct (THEOCHEM)* 583:69–72
 28. Frenkel M, Kabo GJ, Marsh KN, Roganov GN, Wilhoit RC (1994) Thermodynamics of organic compounds in the gas state, vol II. Thermodynamic Research Center, College Station, TX
 29. Matus Myrna H, Arduengo AJ III, Dixon DA (2006) The heats of formation of diazene, hydrazine, N₂H₃⁺, N₂H₅⁺, N₂H, and N₂H₃ and the methyl derivatives, CH₃NNH, CH₃NNCH₃, and CH₃HNNHCH₃. *J Phys Chem A* 110:10116–10121
 30. Byrd CEF, Rice BM (2006) *J Phys Chem A* 110:1005–1013
 31. Kamlet MJ, Adolph HG (1979) Stoichiometric means of assessing impact sensitivity through correlations with oxygen balance. *Propellants Explos Pyrotech* 4:30–34
 32. Ou YX, Chen JJ (2005) The high energy and density compounds, 1st edn. National Defense Industry Press, Beijing
 33. Xiao HM, Xu XJ, Qiu L (2008) Theoretical design of high energy density materials. Science, Beijing