



Theoretical Study on Structures and Properties of High-Energy Density Derivatives of Pyridine

PENG LIAN, WEI-PENG LAI*, BO-ZHOU WANG, XI-JIE WANG and YI-FEN LUO

Xi'an Modern Chemistry Research Institute, Xi'an 710065, P.R. China

*Corresponding author: Tel: +86 29 88291050; E-mail: laneph@126.com

Received: 24 June 2013;

Accepted: 17 October 2013;

Published online: 15 April 2014;

AJC-15025

The geometries of pyridine and its eight derivatives have been fully optimized at the level of B3LYP/6-31G**. The vibration frequencies, nature bond orbits and IR spectra have been calculated at the same level. The results show that the introduction of energetic groups, such as -NO and -C(NO₂)₂, will elongate the C-C bonds and shorten C-N bonds of pyridine rings at same time and the interaction of π orbit and the adjacent π^* orbit can improve the stability of pyridine ring. The stretching vibration bands of pyridine rings show bathochromic shift after the groups introduced as the result of conjugation effect. Their density, detonation velocity and detonation pressure are predicted, and the results show they are high-energy-density compounds. The properties are proportional to number of -NO₂ or -NO in the ring.

Keywords: Pyridine derivative, Density functional theory, Structure, Property.

INTRODUCTION

The high-energy-density derivatives of pyridine have become the focus of chemist's attention in recent years because of their high energy, insensitivity and heat-resistant trait¹⁻⁴. 2,6-Diamino-3,5-dinitropyridine-1-oxide (ANPyO) obtained by Ritter and Licht⁵. It has similar structure with triaminotrinitrobenzene (TATB) melting point over 340 °C, theoretical density of 1.878 g cm⁻³, which makes it one of potential high energy insensitivity explores. 2,4,6-Triamino-3,5-dinitropyridine-1-oxide⁶, one derivative of above mentioned compound with the density of 1.876 g cm⁻³, is a potential insensitive high energy explosive. 2,6-Dipicrylamino-3,5-dinitropyridine (PYX) is another well-known pyridine derivative (density is 1.77 g cm⁻³, detonation velocity is 7448 m s⁻¹, melting point over 350 °C). It is one of the most heat-resistant explosives and has been widely used in the petroleum deep penetrator, explosion exploring of the metagalaxy and nuclear technology *etc.*

In the theoretical study, Zhao and Lu⁷ calculated the densities, heats of formation of seven energetic pyridine derivatives and predicted the detonation properties and thermal stabilities. They found that there were good linear relationships between detonation velocity, detonation pressure and the number of nitro group. Türker *et al.*⁸ calculated the heats of formation for all possible nitro derivatives of pyridine by the application of various density functional theory methods by a proper isodesmic reaction. They suggested that the heat of formation data trends were independent of the selected density functional

theory method. Li *et al.*⁹ calculated the electron structures, molar volumes and thermodynamics properties of 15 polynitropyridine derivatives by the density functional theoretic method. They predicted the crystal structures of 28 polynitropyridine and their oxide and calculated the detonation velocity using stine method. The detonation velocities of 3,5-diamino-2,4,6-trinitropyridine and its oxide are 8.2 and 8.6 km s⁻¹ respectively. The energies are 15 and 25 % higher than them of triaminotrinitrobenzene.

In the present work, 8 high-energy-density pyridine derivatives were selected whose structures are not reported were designed (Fig. 1). Their IR spectra, thermal stabilities and detonation characters were predicted on the basis of optimized geometries to search for the potential high-energy-density compounds.

CALCULATION

Density functional theory B3LYP method (Becke's three-parameter hybrid function¹⁰ with the non-local correlation of Lee *et al.*¹¹ with a 6-31G** basis set were carried out for investigating pyridine (1) and eight derivatives (2-9) using Gaussian 09 program¹². The geometries were fully optimized and the frequency calculations were performed, which indicated that these geometries correspond to be minima (no imaginary frequency) in the potential energy surfaces. The harmonic frequencies and IR spectra were obtained on the basis of vibrational analysis calculations. The Wiberg bond orders were calculated by the analysis of nature bond orbit (NBO).

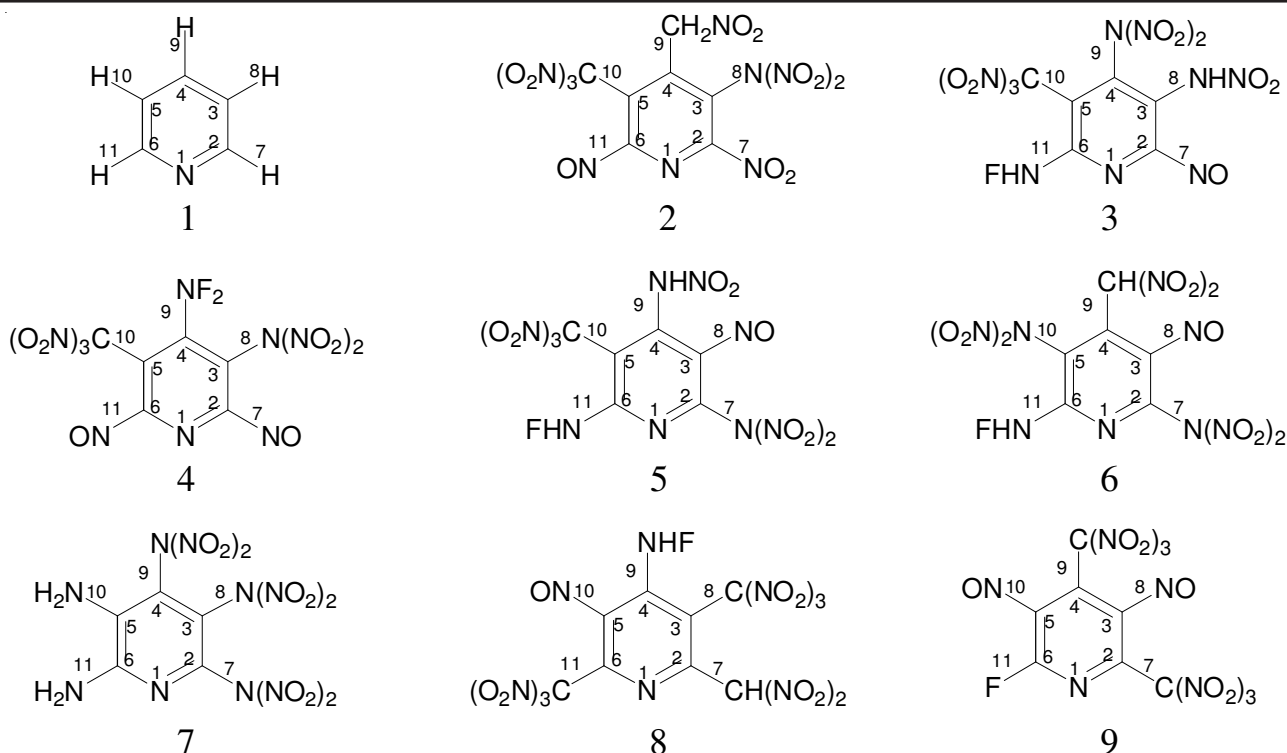


Fig. 1. Structures and atomic numbering of pyridine and derivatives

The density and enthalpy of formation play key role during the design and estimate of energetic materials. In the work, the densities of 8 compounds were predicted by equation $\rho = M/V_m$. Their molar volumes [V_m], which were defined as inside a contour of 0.001 electrons/Bohr³ densities, were evaluated using a Monte Carlo integration. Their solid phase enthalpies of formation [$\Delta H_f(\text{solid})$] can be obtained from the gas phase enthalpies of formation using Hess' law of constant heat summation [eqn. (1)]. The gas phase enthalpies of formation [$\Delta H_f(\text{gas})$] can be calculated at B3LYP/6-31G** level and the enthalpies of sublimation [ΔH_{sub}] can be calculated by eqns. (2-6), which were presented by Politzer *et al.*¹³.

$$\Delta H_f(\text{solids, 298 K}) = \Delta H_f(\text{gas, 298 K}) - \Delta H_{\text{sub}}(298 \text{ K}) \quad (1)$$

$$\Delta H_{\text{sub}}(298 \text{ K, kcal/mol}) = 0.000475 A^2 + 2.1194 (v\sigma_{\text{tot}}^2)^{0.5} - 2.25 \quad (2)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_s^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_s^-]^2 \quad (3)$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (4)$$

$$\bar{V}_s^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (5)$$

$$\bar{V}_s^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (6)$$

where A is the molecular surface area on the specified isosurface, v is balance parameter, $V(r)$ is electrostatic potential, $V(r)$ is the value of $V(r)$ at any point r_i on the surface, $V^+(r_i)$ and $V^-(r_j)$ represent the positive and negative value of $V(r)$ on the surface, \bar{V}_s^+ and \bar{V}_s^- are their averages, σ_{tot}^2 is the total variance. In this paper, A, $V^+(r_i)$ and $V^-(r_j)$ of 8 compounds were calculated at B3LYP/6-31G** level.

In this work, the detonation velocities (D), pressures (p) and heats (Q) of 8 compounds were estimated by the formulae (eqns. (7-11) of Kamlet-Jacobs¹⁴.

$$D = 1.01 (\bar{N}M^{1/2} Q^{1/2}) (1 + 1.30 \rho_0) \quad (7)$$

$$p = 1.558 \rho_0 \bar{N}M^{1/2} Q^{1/2} \quad (8)$$

$$N = (b + 2c + 2d) / 4M \quad (9)$$

$$\bar{M} = (56d + 88c - 8b) / (b + 2c + 2d) \quad (10)$$

$$Q = \frac{28.9b + 94.05(c/2 - b/4) + 0.239 \Delta_f H_m}{M} \quad (11)$$

where ρ_0 is density (g cm⁻³) and M is molecular weight and $\Delta_f H_m$ is standard molar enthalpy of formation (kJ mol⁻¹), that is $\Delta H_f(\text{solid})$ in eqn. (1).

RESULTS AND DISCUSSION

Geometries and nature bond orbits: The B3LYP optimized structure parameters (bond length, bond angle and dihedral angle) are listed in Table-1. It could be seen that the bond length of C-C and C-N bond in pyridine rings (1-9) are 1.307-1.438 Å, which are between the typical single bond length (1.46 Å) and typical double bond length (1.22 Å). It is indicated that the substituents base little effect on the bond

TABLE-1
OPTIMIZED GEOMETRIC PARAMETERS OF PYRIDINE AND DERIVATIVES AT THE B3LYP/6-31G**

Geometric parameters	1	2	3	4	5	6	7	8	9
R(1,2)	1.339 (1.337) ^b	1.307	1.330	1.325	1.320	1.318	1.332	1.340	1.326
R(2,3)	1.396 (1.402)	1.399	1.409	1.406	1.409	1.410	1.388	1.409	1.406
R(3,4)	1.394 (1.392)	1.419	1.420	1.405	1.411	1.406	1.420	1.410	1.418
R(4,5)	1.394 (1.392)	1.418	1.403	1.401	1.415	1.399	1.394	1.395	1.404
R(5,6)	1.396 (1.402)	1.425	1.429	1.423	1.427	1.419	1.438	1.411	1.416
R(6,1)	1.339 (1.337)	1.324	1.317	1.321	1.330	1.337	1.327	1.319	1.315
R(2,7)	1.089	1.495	1.461	1.473	1.435	1.441	1.435	1.518	1.520
R(3,8)	1.086	1.429	1.406	1.427	1.438	1.434	1.416	1.509	1.433
R(4,9)	1.086	1.513	1.418	1.455	1.390	1.505	1.426	1.439	1.522
R(5,10)	1.086	1.517	1.506	1.514	1.492	1.423	1.382	1.444	1.459
R(6,11)	1.089	1.478	1.403	1.471	1.381	1.381	1.367	1.518	1.313
A(1,2,3)	123.8 (123.8)	123.5	123.1	121.9	123.5	123.2	123.7	121.5	123.6
A(2,3,4)	118.4 (118.3)	118.5	116.6	117.2	117.2	117.6	117.4	116.3	119.0
A(3,4,5)	118.6 (118.4)	118.2	119.9	121.4	119.0	119.7	120.1	121.1	116.9
A(4,5,6)	118.4 (118.3)	116.5	116.4	114.8	115.7	117.4	116.5	117.7	117.9
A(5,6,1)	123.8 (123.8)	123.9	122.9	123.7	122.8	122.7	122.9	120.8	124.9
A(6,1,2)	117.1 (117.4)	119.2	119.6	120.2	118.5	119.5	119.2	122.4	117.5
A(1,2,7)	116.0 (116.3)	114.0	110.5	111.1	113.0	113.3	116.8	111.6	115.5
A(2,3,8)	120.3 (120.3)	123.3	121.7	124.8	126.1	127.5	118.8	129.1	112.7
A(3,4,9)	120.7 (120.8)	115.3	120.4	122.0	119.7	121.1	116.3	117.3	120.3
A(4,5,10)	121.3 (121.4)	125.9	125.1	123.3	123.2	118.3	125.8	114.4	117.3
A(5,6,11)	120.2	128.7	117.7	126.2	118.6	125.2	118.5	124.5	119.5
D(1,2,3,4)	0.001	3.011	10.55	6.028	-12.63	0.911	1.138	-3.802	-0.136
D(2,3,4,5)	-0.001	0.443	-3.308	-0.171	1.429	-0.842	-1.146	4.504	-3.208
D(3,4,5,6)	-0.000	-3.976	-7.458	-7.043	13.56	0.653	0.809	-1.627	4.631
D(4,5,6,1)	0.002	4.835	12.97	9.741	-20.40	-0.499	-0.429	-2.289	-3.097
D(5,6,1,2)	-0.001	-1.644	-6.509	-4.529	10.36	0.545	0.390	3.125	-0.281
D(6,1,2,3)	0.000	-2.446	-5.777	-3.793	6.837	-0.759	-0.766	0.052	1.928
D(1,2,3,8)	180.0	-177.7	-175.8	-173.6	155.0	-174.8	-178.6	176.8	-178.3
D(2,3,4,9)	180.0	-176.8	173.9	-176.4	177.0	176.5	174.9	-171.5	176.3
D(3,4,5,10)	180.0	174.7	168.2	173.5	-171.0	-178.3	-178.1	174.7	-167.6
D(4,5,6,11)	180.0	-173.0	-171.5	-165.1	163.3	172.1	178.4	178.4	177.6
D(6,1,2,7)	-180.0	178.1	176.8	176.2	-178.0	-179.7	178.6	-175.5	-177.4

^aR is bond length (Å), A is bond angles (°), D is dihedral angles (°), ^bValues in brackets is experimental values by microwave method¹⁵.

1 = Pyridine; 2-9 = Pyridine derivatives (Fig. 1).

length and the C-C bond adjacent to the substituents are elongated and the C-N bond are shortened.

For pyridine (1), the calculated values of bond lengths and bond angles are consistent with the experimental values from the microwave method.

The Wiberg bond orders of pyridine and derivatives are listed in Table-2. Nature bond orbits analysis results indicate that the bond order values of C-C and C-N bond in pyridine rings are in the range of 1.175-1.442 a.u., which range from the typical single bond order (1 a.u.) to typical double bond order (2 a.u.). The second-order perturbational stabilization energies illustrate that there is a strong interaction between the π orbit and the adjacent π^* orbit and the interaction energies range from 41.20 to 130.54 kJ mol⁻¹. The lone pairs of electrons of N atom in pyridine ring act on the π^* orbits of two adjacent bonds and the energies are in the range of 40.40-51.75 kJ mol⁻¹. The interaction in pyridine ring can improve the stability of pyridine ring.

All bond angles in pyridine rings are approximate to 120° and the highest variational value is 3.6°, which indicated the effects of substituents to bond angles in rings are little. Dihedral angle data show that the pyridine's plane is distorted by substituent and the most variational value of dihedral angle is 20.4°.

Comparing with the corresponding C-C and C-N single bond, the lengths of bond in the ring are shorter and the bonds are more stable because every bond in the ring are nonlocalized. So the relative intensities of the C-C and C-N bonds, which connect the substituents and pyridine rings, require attentions. The bond length data show that the lengths of C-C bonds (1.492-1.522 Å), which link the substituents and pyridine rings, are shorter than the typical C-C bond length (1.540 Å).

Harmonic frequencies and spectra: The calculated infrared spectra (IR) of pyridine and its derivatives are presented in Fig. 2 and the corresponding harmonic frequencies and vibration modes are shown in Table-3.

Bathochromic shifts of the stretching vibration signals from eight pyridine derivatives (2-9) could be observed on the predicted IR spectra as the result of conjugated effect. The vibrational frequency ranges of nitro group (-NO₂) in compounds 2-9 are wide because of the surroundings of nitro group, inductive effect, steric exclusion and so on. The vibrational frequency ranges of nitroso group (-NO) in compounds 2-9 are narrow (1678-1636 cm⁻¹).

Properties: The predicted densities (ρ), solid-phase enthalpies of formation ($\Delta_f H_m$), detonation velocities (D), detonation pressures (p) and heat (Q) of the eight pyridine

TABLE-2
CALCULATED WIBERG BOND ORDER (a.u.) OF PYRIDINE AND ITS DERIVATIVES AT THE B3LYP/6-31G**

Bonds	1	2	3	4	5	6	7	8	9
B(1,2)	1.427	1.439	1.365	1.391	1.427	1.439	1.354	1.358	1.398
B (2,3)	1.430	1.332	1.313	1.312	1.281	1.281	1.374	1.366	1.319
B (3,4)	1.436	1.341	1.297	1.340	1.289	1.316	1.245	1.324	1.299
B (4,5)	1.436	1.376	1.378	1.382	1.324	1.387	1.394	1.358	1.378
B (5,6)	1.430	1.301	1.240	1.277	1.241	1.248	1.175	1.279	1.255
B (6,1)	1.427	1.391	1.422	1.425	1.353	1.330	1.390	1.442	1.405
B (2,7)	0.911	0.864	1.054	1.029	0.972	0.960	0.973	0.989	0.983
B (3,8)	0.911	0.996	1.060	0.990	1.107	1.104	1.006	1.008	1.103
B (4,9)	0.912	1.012	1.017	0.999	1.102	1.002	1.004	1.028	0.998
B (5,10)	0.911	1.010	1.021	1.005	1.027	1.001	1.151	1.083	1.061
B (6,11)	0.911	1.031	1.102	1.031	1.163	1.168	1.199	0.982	0.967

1 = Pyridine; 2-9 = Pyridine derivatives (Fig. 1).

TABLE-3
VIBRATIONAL MODELS AND FREQUENCIES OF PYRIDINE AND ITS DERIVATIVES AT THE B3LYP/6-31G**

Vibrational models	1	2	3	4	5	6	7	8	9
Stretching vibration of ring	1481	1438	1475	1435	1473	1467	1430	1454	1459
	1635	1575	1549	1539	1558	1576	1470	1569	1573
	1641	1603	1627	1612	1604	1610	1616	1622	1595
Flexural vibration of NO ₂	-	778,	774	780	785	778	788	809	810
				834		840	831		
Symmetric stretching vibration of NO ₂	-	1307	1310	1305	1305	1305	1318	1352	1351
		1345	1343	1343	1316	1309	1379	1356	1354
		1350	1355	1351	1351	1374	1379	1356	1413
		1399	1365		1414	1418			
Antisymmetric stretching vibration of NO ₂	-	1685	1688		1662	1695		1689	
		1687	1733	1724	1719	1713	1736	1693	1698
		1700	1743	1740	1738	1739	1774	1698	1722
		1744	1743	1740	1738	1739	1780	1720	1723
		1737	1750	1792	1747	1787	1783	1729	1738
		1809	1804		1785	1791		1736	1742
Symmetric stretching vibration of NO	-	1672	1636	1663	1646	1657	-	1661	1678

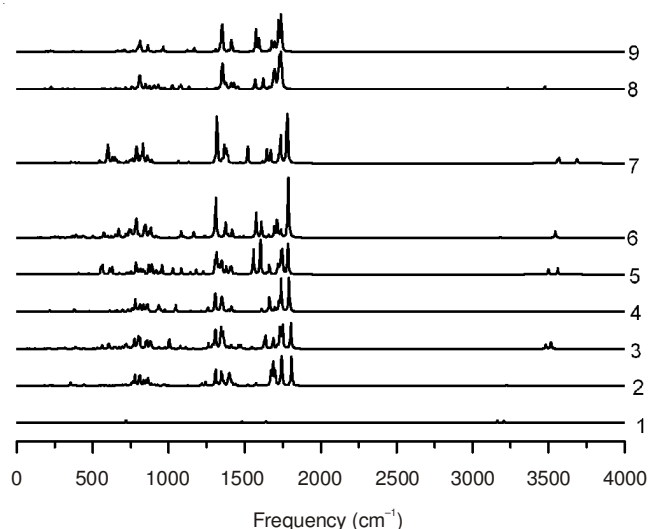


Fig. 2. Calculated IR spectra of pyridine and its derivatives at the B3LYP/6-31G**

derivatives are shown in Table-4. The relationship between the predicted densities, detonation velocities, detonation pressures of pyridine derivatives and the numbers of -NO₂ or -NO group is presented in Fig. 3.

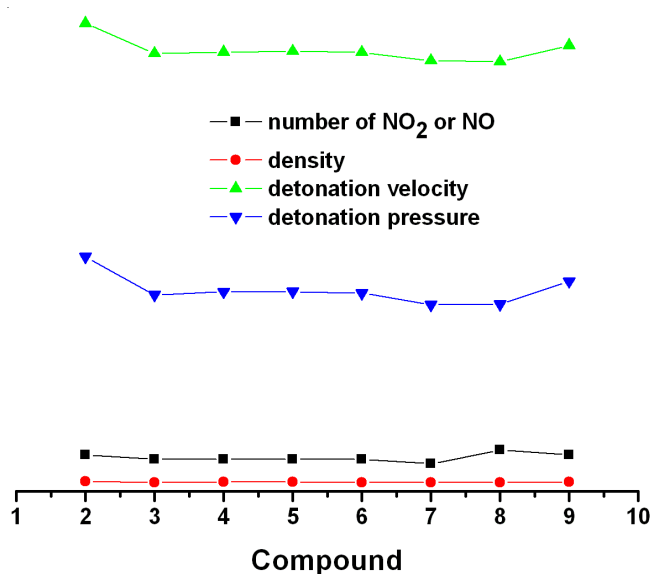


Fig. 3. Relationship between the predicted densities, detonation velocities, detonation pressures of pyridine derivatives and the numbers of -NO₂ or -NO group

As shown in Table-4, the predicted densities of compounds 2-9 are all over 1.9 g cm⁻³ and the predicted detonation velo-

TABLE-4
PREDICTED PROPERTIES OF EIGHT PYRIDINE DERIVATIVES

Pyridine derivatives	ρ (g cm ⁻³)	$\rho_r H_m$ (kJ mol ⁻¹)	D (m s ⁻¹)	p (Gpa)	Q (kJ kg ⁻¹)
2	2.17	391.66	10181.02	51.06	7272.33
3	2.00	400.00	9527.95	42.79	6888.89
4	2.03	479.20	9556.86	43.41	7032.17
5	2.02	377.98	9579.12	43.49	6838.38
6	2.01	390.43	9554.72	43.15	6866.94
7	1.93	381.69	9372.58	40.59	6682.48
8	1.96	283.08	9348.68	40.74	7011.33
9	2.11	221.77	9703.13	45.70	6859.90

cities over 9 km s⁻¹, which makes compounds **2-9** high-energy-density compounds. From Fig. 3, the values of density, detonation velocity and detonation pressure of compounds **2-9** are approximately proportional to the numbers of -NO₂ or -NO group with the exception of compound 8, which might be a result from the steric exclusion of the substituent -C(NO₂)₃ or -CH(NO₂)₂ and incompact arrangement. Consequently, the density decreasing induces the decreasing of detonation velocity and detonation pressure. It could be concluded that the pyridine ring should connect more -NO₂ or -NO groups and the steric exclusion should be little to design a pyridine derivative with high energy. However, the sensitivity of the compound will increase when the number of the energy group increases, which might bring problems for safety handle.

Stability: In order to further investigate the stabilities of the compounds **2-9**, the scan for the potential energy surface was carried out and the transition state and activation energy was obtained. Then the dissociation energies of the easily broken bonds were calculated.

As shown in Table-5, the activation energies of the eight compounds are less than 20 kcal/mol and the dissociation energies are lower than 120 kJ/mol, which indicates that the stabilities of all the eight compounds are poor.

TABLE-5
CALCULATED STABILITIES OF EIGHT
PYRIDINE DERIVATIVES

Pyridine derivatives	Broken bonds	Activation energies (kJ/mol)	Dissociation energies (kJ/mol)
2	8-N-NO ₂	48.97	102.54
	10-C-NO ₂	57.46	59.87
3	10-C-NO ₂	44.22	89.40
	9-N-NO ₂	65.40	77.81
4	10-C-NO ₂	36.89	81.07
5	10-C-NO ₂	50.75	99.86
6	11-N-F	66.00	195.55
	10-N-NO ₂	68.33	73.90
7	7-N-NO ₂	44.64	75.50
	9-N-NO ₂	48.71	50.34
	8-N-NO ₂	50.87	56.63
8	8-C-NO ₂	44.36	71.85
9	9-C-NO ₂	52.19	82.11

Conclusion

In the present work, density functional theory studies were performed for eight potential pyridine derivatives. The stable

geometries of the eight compounds were optimized at B3LYP/6-31G** level. The Wiberg bond orders, harmonic frequencies, IR spectra, activation energies and dissociation energies of the broken bond were calculated theoretically. The densities, solid-phase enthalpies of formation and detonation properties were predicted.

The results show that the effects of substituents to the bond length are little. Strong interaction between the π orbit and the adjacent π^* orbit could be observed. On the other hand, the lone pairs of electrons of N atom in pyridine ring act on the π^* antibonding orbitals of two adjacent bonds and the interaction in pyridine ring can improve the stability of pyridine ring. Bathochromic shifts of the stretching vibration signal from pyridine occur in the eight pyridine derivatives and the vibrational frequency ranges of nitro group are wide because of the surroundings of nitro group, inductive effect, steric exclusion, etc. The result shows eight compounds belong to high-energy-density compounds and their detonation properties are approximately proportional to the numbers of -NO₂ or -NO group. Unfortunately, the stabilities of the eight compounds are poor.

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