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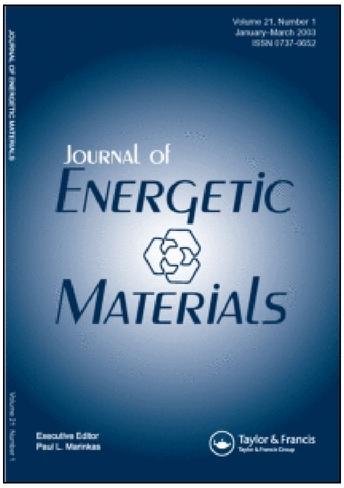

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A Theoretical Study of Polynitropyridines and their *N*-oxides

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A Theoretical Study of Polynitropyridines and Their *N*-oxides

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The geometries of polynitropyridines and their N-oxides have been optimized using the B3LYP density functional method and the 6-311++G** basis set. The accurate gas phase enthalpy of formation (at $p = 1.013 \times 10^5$ Pa and $T = 298.15$ K) for pyridine and its N-oxide has been calculated employing the G3(MP2) method and the atomization scheme, and for polynitropyridines and their N-oxides at the B3LYP/6-311++G** level by designing the isodesmic reactions in which the pyridine ring maintains integral. Based on B3LYP/6-311++G** optimized geometries and calculated natural charges, this paper has calculated the crystal structures by the Karfunkel-Gdanitz method, and based on estimated solid enthalpies of formation and crystal densities has predicted the Chapman-Jouguet detonation velocities (D_{CJ}) by the Stine method. Calculated results show that for polynitropyridines and their N-oxides the introduction of $-NH_2$ groups increases the strength of $C-NO_2$ bonds but reduces the gas phase enthalpy of formation. The least $C-NO_2$ bond order indicates that compounds 3,5-diamino-2,4,6-trinitropyridine and its N-oxide, whose D_{CJ} values are predicted to be

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approximately 8.2 and 8.6 km/s, respectively, are most possibly low-sensitive or insensitive energetic materials. The largest D_{CJ} value obtained in polynitropyridines and their N-oxides is about 9.5 km/s.

Keywords: polynitropyridine, polynitropyridine-1-oxide, enthalpy of formation, impact sensitivity, detonation velocity, B3LYP density functional method

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1. Introduction

Energetic materials have been used in many fields. There is an ongoing need for powerful but insensitive materials. A specific goal [1] is to synthesize the materials that match the performance of the widely used energetic material HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) with the sensitivity of the well-known insensitive energetic material TATB (1,3,5-triamino-2,4,6-trinitro benzene). On the other hand, researchers are trying to determine whether materials exist that are more energetic than present energetic materials.

Because pyridine has aromaticity, larger enthalpy of formation, and higher density, efforts have concentrated on the synthesis of nitro derivatives of pyridine and its *N*-oxide [2]. Recently Holins et al. [3] prepared 2,6-diamino-3,5-dinitropyridine-1-oxide,2,4,6-triamino-3,5-dinitropyridine and its *N*-oxide. In 1988 Licht and Ritter [4] reported the synthesis of 2,4,6-trinitropyridin and its *N*-oxide and recently investigated the syntheses and reactions of dinitrated amino and diamino pyridines [5]. Although a series of nitro derivatives of pyridine and its *N*-oxide have been prepared, to our knowledge, only the performance of 2,4,6-trinitropyridin and its *N*-oxide have been evaluated [4].

To evaluate the performance of polynitropyridines and their *N*-oxides and to seek the novel insensitive energetic materials that satisfy the above-mentioned goal, this work theoretically investigates several important properties of a series of nitro derivatives of pyridine and its *N*-oxide including structure, enthalpy of formation, impact sensitivity, and performance. It is well known that the introduction of the $-NH_2$ group into polynitrobenzenes generally can increase the stability under the stimuli of impact and shock [6,7], so some typical aminonitropyridines and their *N*-oxides have been considered to obtain insensitive candidates. Additionally this paper tries to shed light on the theoretical design of energetic materials.

2. Computational Methods

To investigate polynitropyridines and their *N*-oxides systematically, the compounds studied here are the following: pyridine (**1**), pyridine-1-oxide (**2**), 2-nitropyridine (**3**), 2-nitropyridine-1-oxide (**4**), 3-nitropyridine (**5**), 3-nitropyridine-1-oxide (**6**), 4-nitropyridine (**7**), 4-nitropyridine-1-oxide (**8**), 2,6-dinitropyridine (**9**), 2,6-dinitropyridine-1-oxide (**10**), 3,5-dinitropyridine (**11**), 3,5-dinitropyridine-1-oxide (**12**), 3,5-diamino-2,6-dinitropyridine (**13**), 3,5-diamino-2,6-dinitropyridine-1-oxide (**14**), 2,6-diamino-3,5-dinitropyridine (**15**), 2,6-diamino-3,5-dinitropyridine-1-oxide (**16**), 2,4,6-triamino-3,5-dinitropyridine (**17**), 2,4,6-triamino-3,5-dinitropyridine-1-oxide (**18**), 2,4,6-trinitropyridine (**19**), 2,4,6-trinitropyridine-1-oxide (**20**), 3,5-diamino-2,4,6-trinitropyridine (**21**), 3,5-diamino-2,4,6-trinitropyridine-1-oxide (**22**), 2,3,5,6-tetranitropyridine (**23**), 2,3,5,6-tetranitropyridine-1-oxide (**24**), 4-amino-2,3,5,6-tetranitropyridine (**25**), 4-amino-2,3,5,6-tetranitropyridine-1-oxide (**26**), pentanitropyridine (**27**), and pentanitropyridine-1-oxide (**28**).

Figure 1 shows the atomic numbering of the pyridine ring. The full geometrical optimizations have been performed using the B3LYP density functional method [8,9] and the 6-311++G** basis set, without any symmetry restriction. After geometry optimizations, harmonic vibrational frequencies have been calculated at the B3LYP/6-311++G** level to determine the nature of located stationary points and the thermodynamic properties. Natural population analysis [10,11] has been applied to all B3LYP optimized geometries at the same computational level. The gas phase enthalpies of formation for pyridine and its *N*-oxide have been obtained by the atomization scheme [12] and the G3(MP2) method [13], and those for polynitropyridines and their *N*-oxides have been calculated

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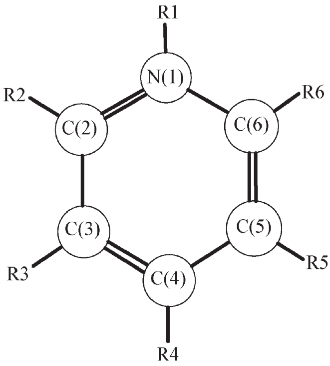

Figure 1. Atomic numbering for the pyridine ring. For polynitropyridine without R1, and for polynitropyridine-1-oxide R1 equal to an O atom.

at the B3LYP/6-311++G** level employing the isodesmic concept [14]. The above quantum chemical calculations have been carried out using the GAUSSIAN 98 W [15] and GAUSSIAN 03 W [16] programs.

The *ab initio* crystal structure calculation method proposed by Karfunkel and Gdanitz [17,18] (hereinafter called the Karfunkel-Gdanitz method) has been used to predict the crystal density and the intermolecular van der Waals energy. Finally the detonation velocity has been evaluated by the Stine method [19].

3. Results and Discussion

3.1. Geometry and Aromaticity

All optimized structures reported here have been characterized to be the minimum of the corresponding potential surface. It is judged from the optimized geometries that compounds **4**, **10**, **14**, **20**, and **22**–**28** are nonplanar, and the others are practically planar. For compounds **23** and **24** the nitro groups in sites 2 and 6 are perpendicular to the pyridine ring, but the ones in sites 3 and 5 are coplanar with the ring. For compounds **10**, **14**, **20**, **22**,

25, and **26** a symmetry plane exists through atoms N(1) and C(4) perpendicular to the ring. The practically existent symmetries are listed in Table 1.

Table 1
Calculated bond length (Å) and variation coefficient (V_{BO}) of bond orders for pyridine ring

Compounds	Symmetry	V_{BO}	N(1)−C(2)	C(6)−N(1)
1	C_{2v}	16.0	1.3368	
2	C_{2v}	14.1	1.3718	
3	C_s	16.1	1.3147	1.3347
4	C_1	14.1	1.3741	1.3779
5	C_s	15.0	1.3333	1.3372
6	C_s	13.2	1.3692	1.3765
7	C_{2v}	15.3	1.3359	
8	C_{2v}	13.6	1.3773	
9	C_{2v}	15.9	1.3137	
10	C_s	14.0	1.3787	
11	C_{2v}	14.4	1.3342	
12	C_{2v}	12.2	1.3742	
13	C_{2v}	13.1	1.3054	
14	C_s	8.7	1.3843	
15	C_{2v}	10.6	1.3368	
16	C_{2v}	8.9	1.3757	
17	C_{2v}	6.5	1.3334	
18	C_{2v}	4.0	1.3682	
19	C_{2v}	15.3	1.3134	
20	C_s	13.4	1.3830	
21	C_{2v}	11.5	1.2993	
22	C_s	5.7	1.3776	
23	C_{2v}	14.2	1.3170	
24	C_{2v}	12.3	1.3785	
25	C_s	12.2	1.3159	
26	C_s	9.8	1.3675	
27	C_1	14.3	1.3124	1.3124
28	C_1	12.0	1.3794	1.3794

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To discuss the aromaticity of polynitropyridines and their *N*-oxides, the variation coefficient (V_{BO}) of the bond orders of the pyridine ring adopted here is [20]

$$V_{\mathrm{BO}} = \frac{100}{\overline{B_O}} \sqrt{\frac{\sum (B_O - \overline{B_O})^2}{n}}, \tag{1}$$

where $\overline{B_O}$ is the arithmetic mean of various bond orders B_O, and n is the number of bonds in the ring. Obviously, for analogues the less V_{BO}, the better the aromaticity. Based on the B3LYP/6-31 ++ G**–calculated atom–atom overlap-weighted NAO bond orders, the variation coefficient of the bond orders of the pyridine ring for polynitropyridines and their *N*-oxides is given in Table 1. The values of V_{BO} for 2,4,6-triamino-3, 5-dinitropyridine-1-oxide, 3,5-diamino-2,4,6-trinitropyridine-1-oxide, and 2,4,6-triamino-3,5-dinitropyridine are 4.0, 5.7, and 6.5, respectively, being much less than others, implying that the aromaticity for the three compounds is better than for others. A look at Table 1 shows that the aromaticity of polynitropyridine is inferior to that of its *N*-oxide.

The calculated C−N bond lengths in the pyridine ring are also included in Table 1. An analysis of Table 1 shows that both N(1)−C(2) and N(1)−C(6) bonds lengthen after the oxidation of polynitropyridines and with $-NO_2$ groups into sites 2, 4, and 6 of pyridine-1-oxide but shrink with $-NO_2$ groups into sites 2, 4, and 6 of pyridine.

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3.2. Impact Sensitivity

It has been pointed out that molecular structure has an influence on susceptibility to shock- and impact-induced reactivity [21,22]. In the area of nitroaromatics a number of studies have been carried out that support the idea that the $C-NO_2$ bond is of key importance in determining impact and shock sensitivities [23–25]. Murray and Politzer [26] suggested that for polynitrobenzenes the electrostatic potentials at the midpoints of $C-NO_2$ bonds are related to impact and shock sensitivities.

Table 2

Least atom–atom overlap-weighted NAO $C-NO_2$ bond order (B_{min}) calculated at B3LYP/6-311++G** level and experimental drop height (12B type with hammer mass 2.5 kg) for LLM-105, TNB, MATB, DATB, and TATB

Energetic materials	B_{min}	H_{50} (cm)[a]
TNB	0.782	71
MATB	0.805	141
DATB	0.838	>320
TATB	0.904	>320
LLM-105	0.808	117

[a] H_{50} for TNB and MATB from [7] and for LLM-105 from [27].

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In this paper the bond order is used to characterize the strength of the $C-NO_2$ bond. Table 2 gives the least B3LYP/6-311 ++ G** atom–atom overlap-weighted NAO bond order (B_{min}) of $C-NO_2$ bonds and the experimental drop height (H_{50}) for TNB(1,3,5-trinitrobenzene), MATB(1-amino–2,4,6-trinitrobenzene), DATB (1,3-diamino-2,4,6-trinitrobenzene), TATB(1,3,5-triamino-2,4,6-trinitrobenzene), and LLM-105(2,6-diamino-3,5-dinitropyrazine-1-oxide). A look at Table 2 displays that H_{50} increases generally with the increase of B_{min}, implying that for aminonitroaromatics B_{min} is related to impact sensitivity.

For polynitropyridines and their *N*-oxides studied here it is postulated that the weakest $C-NO_2$ bond is the trigger bond of deflagration under the stimuli of impact and shock. The calculated atom–atom overlap-weighted NAO bond orders and the bond lengths (r) for $C-NO_2$ bonds are listed in Table 3. When two amino groups are introduced into 2,4,6-trinitropyridine and its *N*-oxide, the values of B_{min} increase by 0.051 and 0.038, respectively. A more detailed analysis of Table 3 shows that for polynitropyridines and their *N*-oxides the introduction of $-NH_2$ groups can strengthen $C-NO_2$ bonds.

Table 3
Calculated atom–atom overlap-weighted NAO bond orders and bond lengths (Å) of C$-$NO$_2$ bonds for polynitropyridines and their *N*-oxides

	C(2)$-$NO$_2$		C(3)$-$NO$_2$		C(4)$-$NO$_2$	
Compounds	B_O	r	B_O	r	B_O	r
3	0.755	1.510				
4	0.780	1.472				
5			0.800	1.477		
6			0.787	1.485		
7					0.782	1.487
8					0.818	1.464
9	0.755	1.509				
10	0.789	1.475				
11			0.792	1.481		
12			0.780	1.489		
13	0.810	1.477				
14	0.834	1.453				
15			0.856	1.448		
16			0.841	1.451		
17			0.913	1.426		
18			0.905	1.428		
19	0.752	1.511			0.772	1.494
20	0.785	1.478			0.803	1.472
21	0.803	1.485			0.876	1.447
22	0.823	1.460			0.893	1.437
23	0.751	1.496	0.785	1.484		
24	0.762	1.487	0.774	1.492		
25	0.747	1.501	0.820	1.467		
26	0.757	1.491	0.814	1.472		
27[a]	0.754	1.501	0.770	1.488	0.761	1.494
28[a]	0.767	1.486	0.761	1.496	0.779	1.485

[a] For compounds **27** and **28** the bond order for C(2)$-$NO$_2$ is equal to that of C(6)$-$NO$_2$, and for C(3)$-$NO$_2$ equal to that of C(5)$-$NO$_2$.

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The values of B_{min} for compounds **17** and **18** are larger than for TATB, implying they are insensitive energetic materials, which is consistent with the experimental results. Although compounds **21** and **22** have not been synthesized up to now, it is meaningful to discuss their impact sensitivity theoretically. The value of B_{min} for compound **21** is slightly less than for MATB, but for compound **22** it approaches that of DATB, implying that compounds **21** and **22** are low-sensitive or insensitive energetic materials.

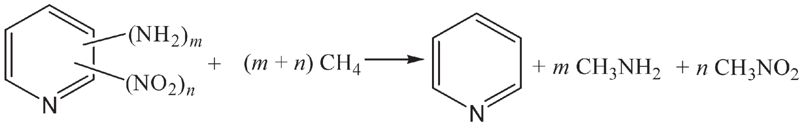
3.3 Gas Phase Enthalpy of Formation

In this work the gas phase enthalpies of formation [ΔH_f^0(g)] for pyridine and its *N*-oxide have been obtained using the G3(MP2) method and the atomization scheme. Table 4 gives the G3(MP2) calculated enthalpies and the experimental enthalpies of formation for C, H, N, and O. The calculated value of ΔH_f^0(g) for pyridine is 138.6 kJ/mol, approaching the experimental value 140 kJ/mol [29], and for pyridine-1-oxide it is 127.4 kJ/mol. For polynitropyridines and their *N*-oxide

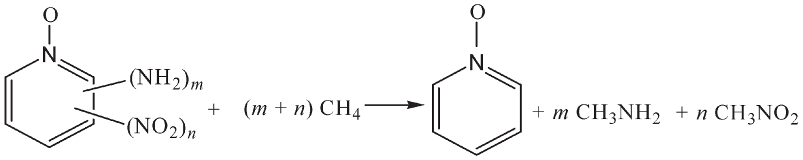
Table 4
G3(MP2) calculated enthalpies (hartree) for C, H, N, and O, B3LYP/6-311++G** calculated enthalpies (hartree) for reference compounds, and experimental enthalpies of formation (kJ/mol) [28] for elements and compounds at $p = 1.013 \times 10^5$ Pa and $T = 298.15$ K

Compounds	H^0	ΔH_f^0 (g)
$C(1s^22s^22p^2)$	−37.786978	716.7
$H(1s^1)$	−0.499478	218.0
$N(1s^22s^22p^3)$	−54.522833	472.7
$O(1s^22s^22p^4)$	−74.987414	249.2
CH_4	−40.485608	−74.8
CH_3NH_2	−95.825720	−23.0
CH_3NO_2	−245.036711	−74.7

it is very expensive to use the G3(MP2) method to calculate their enthalpies of formation, so the isodesmic concept has been adopted. The isodesmic reactions are designed as follows, in which the pyridine ring maintains integral:



(2)



(3)

By calculating the enthalpies (H^0) at the B3LYP/6-311++G** level and employing the experimental enthalpies of formation of reference compounds (CH_4, CH_3NH_2, and CH_3NO_2) (see Table 4) at $p = 1.013 \times 10^5$ Pa and $T = 298.15$ K, the gas phase enthalpies of formation for polynitropyridines have been calculated by reaction (2) and for their *N*-oxide by reaction (3). The $\Delta H_f^0(\mathrm{g})$ values obtained in this work are listed in Table 5.

A glance at Table 5 displays that the gas phase enthalpy of formation for polynitropyridine is less than for its *N*-oxidize and that pentanitropyridine-1-oxide holds the largest gas phase enthalpy of formation (392.2 kJ/mol). The gas phase enthalpy of formation for 2,4,6-trinitropyridine is 154.4 kJ/mol, but for 3,5-diamino-2,4,6-trinitropyridine is 83.8 kJ/mol, so the introduction of the amino group lessens the enthalpy of formation, although it can desensitize the compounds.

3.4. Crystal Structure and Performance

The Chapman-Jouguet detonation velocity (D_{CJ}) is generally proportional to density, so crystal density (ρ) is an important

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Table 5
Calculated enthalpies (hartree) and gas phase enthalpies (kJ/mol) of formation for polynitropyridines and their *N*-oxides at $p = 1.013 \times 10^5$ Pa and $T = 298.15$ K

Compounds	H^0	$\Delta H_f^0(g)$
1	−248.257657	138.6
2	−323.441850	127.4
3	−452.812708	128.3
4	−527.979025	164.1
5	−452.812117	129.9
6	−527.991647	130.9
7	−452.811549	131.4
8	−527.997563	115.4
9	−657.361696	134.0
10	−732.511838	212.2
11	−657.360534	137.0
12	−732.536346	147.8
13	−768.098436	89.2
14	−843.242581	183.2
15	−768.123802	22.6
16	−843.300778	30.4
17	−823.493841	−4.2
18	−898.670218	5.2
19	−861.905064	154.4
20	−937.058272	224.5
21	−972.651642	83.8
22	−1047.795321	178.9
23	−1066.426610	232.1
24	−1141.579914	302.0
25	−1121.799748	197.2
26	−1196.945423	287.1
27	−1270.944676	318.9
28	−1346.096797	392.2

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physical quantity for energetic materials. The Karfunkel-Gdanitz method contained in the Cerius^2 software [30] allows us to predict the crystal structure from molecular structure. In this paper the Dreiding force field [31] that models carbon, nitrogen, oxygen, and hydrogen accurately is adopted, and the 17 most common space groups [32] are considered. In the Monte Carlo packing simulation, heating and cooling factors are set to 0.01 and 0.001, respectively. The asymmetric unit contains one rigid unit. The calculated results for the five lowest total energies of the 17 space groups are summarized in Table 6, where the solid enthalpy of formation $\Delta H_f^0(\mathrm{s})$ is the gas phase enthalpy of formation plus the intermolecular van der Waals energy (ΔE_{VDW}). Based on calculated ρ and $\Delta H_f^0(\mathrm{s})$, D_{CJ} has been estimated using the Stine method:

$$D_{\mathrm{CJ}} = D_0 + \rho(c_1 n_{\mathrm{C}} + c_2 n_{\mathrm{N}} + c_3 n_{\mathrm{O}} + c_4 n_{\mathrm{H}} + c_5 \Delta H_f^0(\mathrm{s}))/M, \quad (4)$$

where D_0 is the characteristic velocity (3.69 km/s) of a void, c_i ($i = 1, 2, 3, 4, 5$) are constants ($c_1 = -13.85$, $c_2 = 37.74$, $c_3 = 68.11$, $c_4 = 3.95$, and $c_5 = 0.1653$), ρ is in Mg/m^3, $\Delta H_f^0(\mathrm{s})$ is in kJ/mol, n_{C}, n_{N}, n_{O}, and n_{H} are numbers of atoms C, N, O, and H, respectively, and M is molecular mass. In general, the Stine method is slightly more accurate than the Kamlet-Jacobs method [33] for CHNO energetic materials. Calculated ΔE_{VDW}, $\Delta H_f^0(\mathrm{s})$, ρ, and D_{CJ} are listed in Table 6.

For compound **17** the calculated density with the $P2_1/c$ space group is very close to the experimental value (1.819 g/cm^3) [3], but for compound **18** it is 0.058 g/m^3 larger than the experimental value (1.876 g/cm^3) [3]. The experiment density for compound **19** (1.77 g/cm^3) [4] is slightly less than the calculated value (about 1.81 g/cm^3), and for compound **20** (1.86 g/m^3) [4] it is slightly larger than the calculated range 1.817–1.853 g/cm^3. The calculated density using the above method is relatively reliable. From Table 6 one can see that the largest D_{CJ} value of polynitropyridines and their N-oxides is about 9.5 km/s, larger than that (about 9.1 km/s) of HMX and close to that (about 9.5 km/s) of CL-20.

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Table 6

Calculated intermolecular van der Waals energies (kJ/mol), solid enthalpies of formation (kJ/mol), densities (g/cm^3), and Chapman-Jouguet detonation velocities (km/s) for polynitropyridines and their *N*-oxides

Compounds	Space group	ΔE_{VDW}	ΔH_f^0(s)	ρ	D_{CJ}
17	$P2_1/c$	−78.7	−82.9	1.813	7.41
	$P\overline{1}$	−90.4	−94.6	1.895	7.57
	$Pbca$	−78.2	−82.4	1.819	7.43
	$Pnma$	−83.7	−87.9	1.780	7.34
	$P1$	−90.4	−94.6	1.895	7.57
18	$P2_1/c$	−94.6	−89.4	1.934	7.95
	$P2_12_12_1$	−96.2	−91.0	1.954	7.99
	$P2_1$	−90.8	−85.6	1.917	7.92
	$Pna2_1$	−92.9	−87.7	1.930	7.94
	$Pca2_1$	−87.4	−82.2	1.892	7.87
19	$P2_1/c$	−102.9	51.5	1.809	7.97
	$P2_12_12_1$	−102.9	51.5	1.807	7.97
	$P2_1$	−101.7	52.7	1.805	7.97
	$C2/c$	−101.7	52.7	1.800	7.95
	$P2_12_12$	−102.5	51.9	1.799	7.95
20	$P2_1/c$	−104.6	119.9	1.840	8.38
	$P\overline{1}$	−106.7	117.8	1.853	8.42
	$P2_12_12_1$	−102.5	122.0	1.821	8.33
	$P2_1$	−103.3	121.2	1.817	8.32
	$C2/c$	−104.6	119.9	1.847	8.40
21	$P2_1/c$	−99.2	−15.4	1.909	8.22
	$P\overline{1}$	−105.9	−22.1	1.911	8.22
	$P2_12_12_1$	−107.5	−23.7	1.945	8.30
	$P2_1$	−101.7	−17.9	1.903	8.20
	$Pna2_1$	−105.0	−21.2	1.898	8.19

(*Continued*)

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Table 6
Continued

Compounds	Space group	ΔE_{VDW}	$\Delta H_f^0(\mathrm{s})$	ρ	D_{CJ}
22	$P2_1/c$	–108.8	70.1	1.950	8.65
	$P\overline{1}$	–106.3	72.6	1.950	8.65
	$P2_12_12_1$	–105.4	73.5	1.922	8.58
	$P2_1$	–105.9	73.0	1.939	8.63
	$Pna2_1$	–107.1	71.8	1.927	8.59
25	$P2_1/c$	–109.6	87.6	1.945	8.83
	$P\overline{1}$	–113.0	84.2	1.993	8.96
	$P2_12_12_1$	–110.0	87.2	1.954	8.86
	$P2_1$	–110.0	87.2	1.951	8.85
	Cc	–105.0	92.2	1.921	8.77
26	$P2_1/c$	–108.8	178.3	1.950	9.12
	$P\overline{1}$	–107.1	180.0	1.956	9.14
	$C2/c$	–108.4	178.7	1.968	9.17
	$Pbca$	–111.7	175.4	1.978	9.19
	Cc	–105.4	181.7	1.930	9.07
27	$P\overline{1}$	–111.7	207.2	1.958	9.31
	$P2_1$	–111.3	207.6	1.959	9.31
	$C2/c$	–110.5	208.4	1.953	9.30
	$Pna2_1$	–109.6	209.3	1.956	9.31
	$Pca2_1$	–109.2	209.7	1.936	9.25
28	$P2_1/c$	–110.9	281.3	1.952	9.50
	$P\overline{1}$	–113.4	278.8	1.968	9.55
	$P2_1$	–110.0	282.2	1.940	9.47
	$C2/c$	–110.5	281.7	1.938	9.46
	$Pbca$	–113.4	278.8	1.975	9.57

The calculated density for compound **21** is in the range 1.898–1.945 g/cm^3 and for compound **22** in the range 1.922–1.950 g/cm^3, implying the two candidates have larger density. The D_{CJ} values for compounds **21** and **22** are predicted to be about 8.2 and 8.6 km/s accounting for 90.1% and 94.5% of detonation velocity of HMX, respectively.

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4. Conclusions

The geometries for polynitropyridines and their *N*-oxides have been optimized at the B3LYP/6-311 ++ G** level. The accurate gas phase enthalpies of formation (at $p = 1.013 \times 10^5$ Pa and $T = 298.15$ K) for pyridine and its *N*-oxide have been calculated employing the G3(MP2) method and the atomization scheme, and for polynitropyridines and their *N*-oxides at the B3LYP/6-31 ++G** level by designing the isodesmic reactions in which the pyridine ring maintains integral. From B3LYP/6-311++G** optimized structures and calculated natural atomic charges the crystal structures have been predicted with the Karfunkel-Gdanitz method. Based on calculated ρ and ΔH_f^0(s), D_{CJ} has been predicted with the Stine method.

The aromaticity of the pyridine ring of polynitropyridine is inferior to that of its *N*-oxide. After oxidation of polynitro pyrazines, both N$-$C bonds in the pyridine ring lengthen. The least C$-$NO$_2$ bond order indicates that compounds 3,5-diamino-2,4,6-trinitropyridine and 3,5-diamino-2,4,6-trinitropyridine-1-oxide are most possibly low-sensitive or insensitive. The predicted D_{CJ} values for 3,5-diamino-2,4,6-trinitropyridine and 3,5-diamino-2,4,6-trinitro pyridine-1-oxide are about 8.2 and 8.6 km/s, respectively. For polynitropyridines and their *N*-oxides, the introduction of the amino group reduces the gas phase enthalpy of formation, although it can desensitize the compounds. By comparison with the experimental values the calculated density using the Karfunkel-Gdanitz method and the Dreiding force field is reliable. The largest D_{CJ} value of polynitropyridines and their *N*-oxides is about 9.5 km/s, approaching that of CL-20.

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