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Theoretical studies of -NH$_2$ and -NO$_2$ substituted dipyridines

Hui Liu · Fang Wang · Gui-Xiang Wang · Xue-Dong Gong

Abstract In this work, the experimental synthesized bipyridines 3,3′-Dinitro-2,2′-bipyridine (DNBPy), 3,3′-Dinitro-2,2′-bipyridine-1,1′-dioxide (DNBPyO), and (3-Nitro-2-pyridyl)(5-nitro-2-pyridyl) amine (NPyA), and a set of designed dipyridines that have similar frameworks but different linkages and substituents with NPyA were studied theoretically at the B3LYP/6-31G* level of density functional theory. The gas-phase heats of formation were predicted based on the isodesmic reactions and the condensed-phase heats of formation and heats of sublimation were estimated in the framework of the Politzer approach. The crystal densities have been computed from molecular packing. Results show that this method gives a good estimation of density in comparison with the available experimental data for DNBPy, DNBPyO, and NPyA. The predicted detonation velocities and pressures indicate that the performance of dipyridines linked with -O-, -NH-, or -CH$_2$-bridges have not been improved compared with that of the directly linked dipyridines, but all derivatives have better detonation properties than DNBPy, DNBPyO, and NPyA because of the presence of more nitro groups. An analysis of the bond dissociation energies (BDEs) or the impact sensitivity (h_{50}) suggests that introduction of different bridges but not substituents has little influence on thermal stability. The calculated h_{50} may be more reliable than BDE for predicting stability. Four bridged bipyridines have quite good detonation performance and low sensitivity.

Keywords Bridged bipyridine · Density · Density functional theory · Detonation properties · Sensitivity

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Introduction

Nitrogen heterocyclic compounds are potential and promising candidates for high-energy density materials (HEDMs) owing to their rather high density, high positive heat of formation, good oxygen balance, and good thermal stability [1]. They have received a great amount of interest in recent years [2–8].

Pyridine is a six-membered heterocyclic compound. The derivatives of pyridine have higher nitrogen contents than the carbocyclic analogues, enabling these compounds to release more nitrogen gases and in turn higher energy in explosion. On the other hand, since a N atom contributes more to the density than a C atom, the presence of pyridine in molecule is supposed to improve its density and correspondingly increase the detonation velocity and pressure [9]. Therefore, the search for new HEDMs containing pyridine has attracted much attention [10–20]. Some substituted pyridine derivatives have been synthesized and investigated for energetic applications [10–13, 21–26]. Some of them, for example, polynitropyridines like 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) have been applied as energetic materials.

To meet the continuing demand for improved energetic materials, there is a clear need to continue to design and develop new pyridine-based HEDMs. Studies on dibenzene linked by -N=N- (i.e., HNAB) [27] or

-CH=CH- (i.e., HNS) [28], and difurazan and ditriazine linked by -NH-NH-, -N=N-, –CH$_2$-CH$_2$-, or -CH=CH- [29, 30] showed they have better detonation performance than monocyclic derivatives. This indicates that the combination of nitrogen heterocycles (or benzene ring) with different bridges may be helpful for improving the performance of energetic materials. In literatures, the bridged bipyridines compounds, e.g., 3,3′-Dinitro-2,2′-bipyridine (DNBPy), 3,3′-Dinitro-2,2′-bipyridine-1,1′-dioxide (DNBPyO), (3-Nitro-2-pyridyl)(5-nitro-2-pyridyl)amine (NPyA) and 2,2′-Oxy-bis(pyridine) (OBy) have been synthesized and reported [31–34]. Although they are not used for energetic materials, their performance can be tuned by introducing some energetic groups. In this study, systematic theoretical studies on the structures, heats of formation, energetic properties, and thermal stability of them and their derivatives with linkages of none (series A), -NH- (series B) , -CH$_2$- (series C), -O- (series D) and substituents of H (series 1), -NH$_2$ (series 2), and -NO$_2$ (series 3) (see Fig. 1) have been performed. Our main purpose here is to investigate the effect of different linkages and substituents on the structure and performance and their roles in the design of efficient high-energy density compounds.

Computational methods

The density functional theory (DFT) B3LYP method [35, 36] in combination with the 6-31G* [37] basis set which has been proved [38–44] to be able to give quite

reliable energies, molecular structures, and other properties was used to fully optimize the molecular geometries of the title compounds with the Gaussian03 program package [45]. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the program. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies.

Detonation velocity and pressure, the most important parameters for evaluating the detonation characteristics of energetic materials, were calculated using the following Kamlet-Jacobs (K-J) equations [46, 47], which have been verified by many studies [38–44] to be suitable for organic explosives.

$$D = 1.01\left(N\overline{M}^{1/2}Q^{1/2}\right)^{1/2}(1+1.30\rho) \quad (1)$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2}, \quad (2)$$

where P is the detonation pressure (GPa), D is the detonation velocity (km/s), ρ is the packed density (g/cm^3), N is the moles of gas products per gram of explosives, $\overline{M}$ is the average molar weight of detonation products, and Q is the chemical energy of detonation (cal/g). N, $\overline{M}$, and Q are decided according to the largest exothermic principle [44].

The density in the K-J equations was usually calculated by the following equation in the previous studies [48–52]:

$$\rho = \frac{M}{V(0.001)}. \quad (3)$$

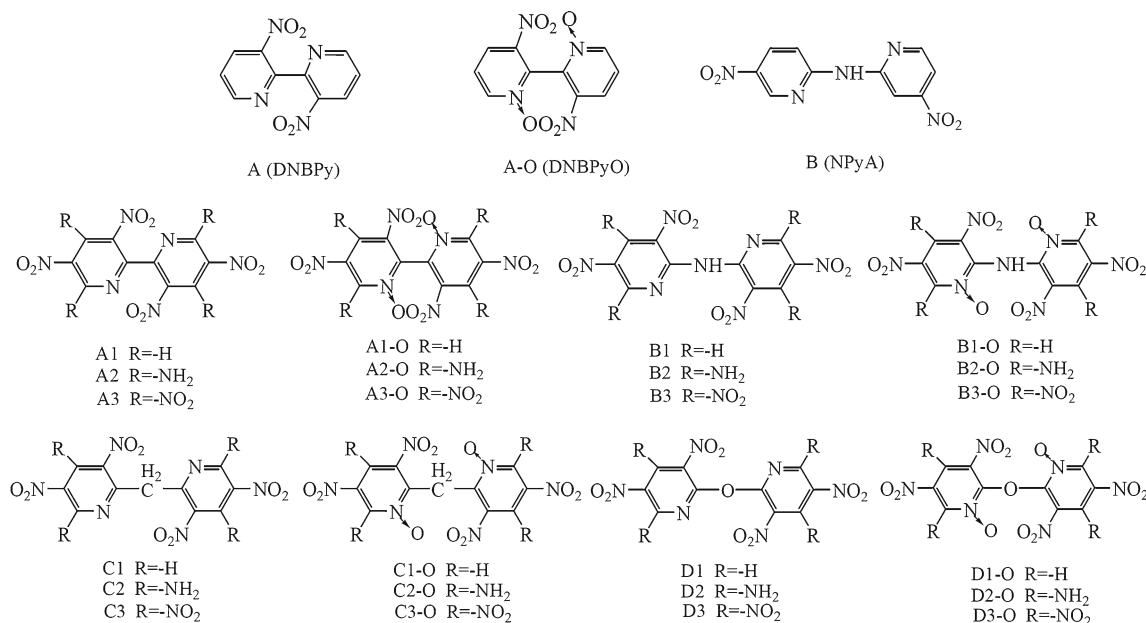In which M is the molecular mass (g/molecule), and $V(0.001)$ is the volume (cm^3/molecule) defined as the

**Fig. 1** The molecular structures of the title compounds

space inside a contour of electron density of $0.001e \cdot$ Bohr^{-3}. However, the results obtained using this equation may have quite big errors for some systems, for example, molecules that can form strong hydrogen bonds. Politzer et al. [53] suggested that Eq. 3 should be corrected to better reflect the effects of intermolecular interactions in crystals. They have proposed two modified equations and the better one is shown as follows [53]:

$$\rho_P = \alpha \left[\frac{M}{V(0.001)} \right] + \beta \left(\nu \sigma_{tot}^2 \right) + \gamma, \tag{4}$$

where α, β and γ are regression coefficients and their values are taken from ref. [53]. ν is the degree of balance between the positive and negative charges on the isosurface, and σ_{tot}^2 is a measure of the variability of electronic potential on the surface [53]. ν and σ_{tot}^2 are calculated using a self-compiled program [54]. Since HEDMs are usually in agglomerate solids, their densities are closer to crystal densities. Therefore, crystal density was also evaluated by the rigorous molecular packing calculations using the polymorph module of Materials Studio [55]. Molecular mechanics method (MM) and the Dreiding force field [56] which is capable for predicting the condensed phase properties were adopted. Since more than 80 % organic compounds crystallize in seven space groups (P2$_1$/c, P-1, P2$_1$2$_1$2$_1$, P2$_1$, Pbca, C2/c, and Pna2$_1$) on the basis of statistical data [57–59], the search of the possible crystal structure has been confined to these most typical groups only.

In this paper, the above mentioned three methods have been used to predict the density of the compounds (A, A-O, B) with experimental values for comparison and evaluation of the methods. The best one was adopted to predict the density of other compounds.

The detonation heat Q was evaluated from the heats of formation (HOFs) of products and reactant. The standard gas-phase HOFs ($\Delta H_f(g)$) of bridged pyridines were calculated using the following isodesmic reactions.

$$(5)$$

$$(6)$$

$$(7)$$

$$(8)$$
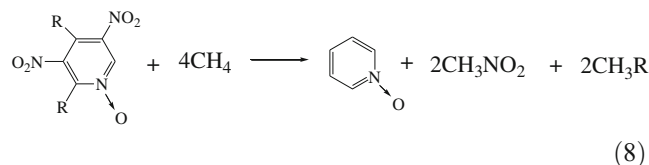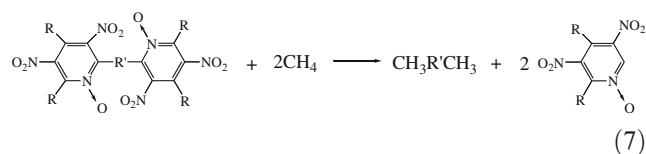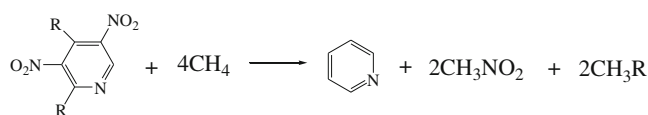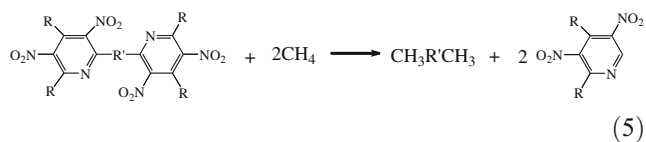
$$R = -H, -NH_2, -NO_2; \ R' = -NH-, -CH_2-, -O-$$

The enthalpy of reaction (ΔH_{298}) of these reactions at 298 K can be calculated from Eq. (9),

$$\Delta H_{298} = \sum \Delta H_f(g, P) - \sum \Delta H_f(g, R)$$
$$= \sum H(P) - \sum H(R), \tag{9}$$

where $\Delta H_f(g, R)$ and $\Delta H_f(g, P)$ are the HOFs and $H(R)$ and $H(P)$ are the enthalpies of the reactants and the products at 298 K, respectively. The experimental HOFs of the reference compounds in isodesmic reactions, CH$_4$, C$_5$H$_5$N, CH$_3$CH$_3$, CH$_3$NHCH$_3$, CH$_3$CH$_2$CH$_3$, CH$_3$OCH$_3$, CH$_3$NO$_2$, and CH$_3$NH$_2$ are available [60]. For the reference compound C$_5$H$_5$NO which lacks experimental HOF, G2 theory [61] has been used to obtain its accurate $\Delta H_f(g)$. When the enthalpies of all compounds and HOFs of all reference compounds are known, the $\Delta H_f(g)$ of the title compounds is readily obtained.

The HOF in solid state ($\Delta H_f(s)$) can then be estimated using Eq. 10

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub}, \tag{10}$$

where ΔH_{sub} is the heat of sublimation evaluated using Eq. 11 suggested by Rice and Politzer et al. [62, 63]:

$$\Delta H_{sub} = \alpha_1 (A_s)^2 + \beta_1 \left(\nu \sigma_{tot}^2 \right)^{0.5} + \gamma_1, \tag{11}$$

where A_s is the surface area of the 0.001 electron/bohr^3 isosurface of the electron density. The values of coefficients α_1, β_1, and γ_1 are taken from ref. [62].

To measure the strength of the bonds and relative stability of the title compounds, the bond dissociation energies (BDEs) of the weak bonds according to the NBO analysis are calculated. BDE is the energy required for a bond homolysis. The expressions for the homolysis of the bond A-B (Eq. 12) and for calculating its BDE (Eq. 13) are shown as follows [64]:

$$A - B(g) \rightarrow A\bullet(g) + B\bullet(g) \tag{12}$$

$$BDE_{(A-B)} = [E_{A\bullet} + E_{B\bullet}] - E_{(A-B)}, \tag{13}$$

where A• and B• are the radicals produced by dissociation of A-B. $BDE_{(A-B)}$ is the BDE of the bond A−B; $E_{(A-B)}$, $E_{A\bullet}$, and $E_{B\bullet}$ are the zero-point-corrected total energies of the parent compound and the corresponding radicals, respectively.

The impact sensitivity (h_{50}), another parameter that can reflect the stability of the compounds, has been estimated using Eq. 14 suggested by Pospisil et al. [65]:

$$h_{50} = \alpha 2\sigma_+^2 + \beta_2 v + \gamma_2, \tag{14}$$

where the values of coefficients α_2, β_2 and γ_2 are taken from ref. [65].

Results and discussion

Heats of formation

Heat of formation is frequently taken to be indicative of the "energy content" of an energetic compound. Therefore, it is important to predict the heat of formation accurately. Previous studies indicated that the calculated values of HOF by applying the isodesmic reactions agree well with experimental values when appropriate reference compounds have been chosen [42, 49, 62, 66, 67]. Table 1 summarizes the $\Delta H_f(g)$ and $\Delta H_f(s)$ of the title compounds and the related data of A_s, v, σ_{tot}^2, and ΔH_{Sub}.

It can be seen from Table 1 that $\Delta H_f(g)$ and $\Delta H_f(s)$ of all the compounds are large and positive except the compounds of series 2 (A2, B2, C2, D2, and their oxides). The substituent -NO_2 increases HOF greatly and -NH_2 decreases HOF a lot, which indicates the nitro group but not the amino group is an effective group for increasing HOF. On the other hand, with the increase in the number of the nitro groups, HOF does not always increase, i.e., HOF does not obey the group additivity rule for these compounds. For example, from A to A1, A-O to A1-O, or B to B1, the nitro number increases from 2 to 4 but the HOF decreases a little. It can also be seen the HOFs of N-oxides are higher than the corresponding pyridines, which indicates oxidation of the pyridine N improves HOF effectively. The HOFs of the bridged dipyridines are all lower than those of the directly linked dipyridines, for example, the HOFs of A1, B1, C1, and D1 are 198.50, 153.92, 172.97, and 46.54 kJ mol^{-1}, while that of A is 241.93 kJ mol^{-1}. The -O- bridge decreases HOF most. This is because when -O- bridge replaces two H, less H_2O and more O_2 will be produced on detonation. This implies that incorporation of -CH_2-, -NH-, or -O- into dipyridines is unfavorable for increasing HOF.

Crystal density

It is well known that density is critical to the detonation properies of energetic materials [46]. In this study, we

compared the densities calculated with Eqs. 3 and 4 and from MM for A, A-O and B with the experimental densities [31–33]. The results are listed in Table 2.

The relative errors of the calculated values to the experimental results show that ρ_c from MM method agree better with the experimental ones than ρ from Eq. 3 and ρ_p from Eq. 4. The mean relative errors of ρ, ρ_p, and ρ_c are 2.49 %, 2.72 %, and 0.63 %, respectively, which means MM method may be more reliable for predicting the crystal density of the title compounds. Thus, the densities of all title compounds have been calculated with the MM method. The predicted crystal structures are shown in appendix. Results of density are collected in Table 3 and show that all compounds have higher densities (1.69~2.08 g/cm^3) than A, A-O, and B. The densities increase with the introducing of -NH_2 and -NO_2, and the latter improves the density more greatly than the former. For example, the densities of A1, A2, and A3 have the order of A3 > A2 > A1. Figure 2 presents a comparison of the densities of all compounds with those of RDX and HMX. It can be seen that the densities of all compounds except A1, B1, C1, C2, C1-O, and D1 are larger than that of RDX and those of A3, A2-O, A3-O, B3, B2-O, B3-O, C3, C3-O, D2, D3, D2-O, and D3-O are even larger than that of HMX. C series with the -CH_2- brigde group have the smallest density (1.69~1.95 g/cm^3) and A, B, and D series have similarly larger density (1.76~2.08 g/cm^3), which indicates incorporation of -CH_2- into dipyridines is unfavorable for increasing the density. What's more, the densities of N-oxides are not always larger than the corresponding parent compounds, which is not consistent with that found for detonation properties.

Detonation properties

Table 3 also collects the predicted heats of detonation (Q), detonation velocity (D) and detonation pressure (P) for the title compounds, along with the experimental results of commonly used explosives RDX and HMX. The relationships between the structures and detonation properies are also plotted in Fig. 2.

The calculated results of Q in Table 3 show that introducing -NO_2 or -NH_2 to A, A-O, and B does not alwalys increase Q. In each A, B, C, and D series, for example, A1, A2, A3 in A series, the substitution derivatives of -NH_2 have smaller and -NO_2 derivatives have larger Q, which shows -NO_2 is more helpful for increasing Q than -NH_2. In adition, the Q of the N-oxides are always larger than the parent compounds. Bipyridines in series 1, 2, 3, or 4 (for example, A1, B1, C1, D1) have close Q values, indicating the effect of bridge groups on Q is small.

It can be found from Fig. 2 that the effects of substitution on the D and P are similar. All derivatives have better detonation properties than A, A-O, and B. The dotonation

Table 1 Calculated heats of formation and related parameters

Compounds	$A_s/(Å^2)$	ν	$\sigma_{tot}^2/(kcal/mol)^2$	$\Delta H_{sub}/(kJ/mol)$	$\Delta H_f(g)/(kJ/mol)$	$\Delta H_f(s)/(kJ/mol)$
A	255.55	0.25	120.25	35.06	276.99	241.93
A-O	264.15	0.25	140.71	38.11	282.96	244.85
B	300.74	0.25	140.59	46.86	246.13	199.27
A1	346.33	0.21	99.93	55.87	254.37	198.50
A2	324.96	0.24	173.07	54.60	43.27	−11.33
A3	441.39	0.04	227.32	83.54	458.66	375.12
A1-O	300.07	0.18	107.95	42.76	278.94	236.18
A2-O	329.15	0.24	139.48	54.06	91.67	37.61
A3-O	358.41	0.04	220.43	55.32	547.90	492.58
B1	317.11	0.22	102.1	48.07	201.99	153.92
B2	327.95	0.04	234.12	46.70	−0.48	−47.18
B3	348.05	0.05	252.67	53.73	413.03	359.30
B1-O	309.58	0.19	111.02	45.69	241.43	195.74
B2-O	327.18	0.25	141.69	53.94	63.11	9.17
B3-O	344.43	0.05	256.11	52.73	511.28	458.55
C1	288.13	0.22	97.78	40.38	213.35	172.97
C2	318.85	0.24	166.58	52.62	16.50	−36.12
C3	345.19	0.05	239.19	52.64	407.81	355.17
C1-O	330.74	0.2	117.3	52.08	240.10	188.02
C2-O	344.39	0.25	146.75	59.11	65.13	6.02
C3-O	366.3	0.04	248.63	58.21	498.33	440.12
D1	307.99	0.21	117.51	46.25	92.79	46.54
D2	330.41	0.24	186.96	56.77	−113.91	−170.68
D3	298.79	0.04	251.48	39.25	301.24	261.99
D1-O	301.84	0.18	105.44	43.08	152.42	109.34
D2-O	397.47	0.24	139.08	75.06	−32.52	−107.58
D3-O	327.95	0.04	234.12	46.70	421.58	374.88

properties of the derivatives in series 1~3 have the order of 3>2>1, which means introducing -NH$_2$ and -NO$_2$ can enhance the detonation properties and -NO$_2$ is more favorable. In addition, the detonation properties of all N-oxides are improved by oxidization. Series A (directly linked) and D (-O- bridged) have larger D and P than series B (-NH- bridged), and compounds in series C (-CH$_2$- bridged) have smallest D and P. This shows that introducing bridge groups (-O-, -NH-, -CH$_2$-) into the directly linked dipyridines does

not improve their denotion properties. The D and P of all compounds in series 3 except C3 are higher than 9.0 km/s and 40.0 GPa, respectively.

From Fig. 2 it is also obvious that the evolution pattern of D or P is very similar to that of ρ. This shows that the detonation properties are predominantly controlled by density. However, there are also dipyridines which have higher ρ but lower D and P than RDX or HMX because of the influence of Q. A3~D3 and their N-oxides have higher D and P than RDX, and all of them except C3 have better detonation performance than HMX too. Furthermore, the detonation performance of A2-O~D2-O is also close to that of RDX. Since the detonation properties of experimental synthesized A, A-O, and B are not perfect, the above mentioned candidates with good performance are worth further experimental investigations.

Thermal stability

Table 4 lists bond order of the relatively weak bonds (BO), bond dissociation enthalpies(BDE), and the characteristic height (h_{50}).

Table 2 Comparison of the densities obtained from various methods[a]

Compounds	$\rho(g/cm^3)$	$\rho_p(g/cm^3)$	$\rho_c(g/cm^3)$	$\rho_{exp}(g/cm^3)$
A	1.61 (2.55)	1.61 (2.35)	1.59 (1.27)	1.57 [31]
A-O	1.70 (3.03)	1.70 (3.27)	1.65 (0.00)	1.65 [32]
B	1.62 (1.89)	1.63 (2.54)	1.60 (0.63)	1.59 [33]
mean error[b]	(2.49)	(2.72)	(0.63)	

[a] ρ, ρ_p, ρ_c, and ρ_{exp} are the densities from Eq. 3, Eq. 4, MM method, and experiment, respectively. Data in the parentheses are the relative errors of the calculated values in percentage. [b] the average relative errors

Table 3 Calculated densities and detonation properties

| Compounds	Space groups	ρ(g/cm³)	Q(kJ/kg)	D(km/s)	P(GPa)
A	$P2_1/c$	1.59	4728.95	5.94	14.49
A-O	$P-1$	1.65	5610.05	6.70	18.89
B	$P-1$	1.60	4380.10	6.00	14.82
A1	$P-1$	1.76	5540.77	7.32	23.46
A2	$P-1$	1.89	4398.95	7.57	26.16
A3	$P-1$	2.08	6825.60	9.36	42.18
A1-O	$P-1$	1.83	6230.35	7.94	28.23
A2-O	$P2_1/c$	1.96	5103.43	8.20	31.36
A3-O	$P2_1/c$	2.04	7359.29	9.49	42.97
B1	$P2_12_12_1$	1.76	5241.14	7.31	23.38
B2	$P2_1/c$	1.84	4205.99	7.40	24.62
B3	$P-1$	2.03	6645.32	9.18	40.10
B1-O	$C2/c$	1.82	5939.52	7.89	27.81
B2-O	$P2_1/c$	1.93	4917.25	8.09	30.24
B3-O	$P-1$	2.00	7142.69	9.34	41.11
C1	$P-1$	1.69	5374.68	7.00	20.91
C2	$P2_1$	1.80	4298.02	7.20	23.01
C3	$P-1$	1.95	6692.43	8.83	36.27
C1-O	$C2/c$	1.79	5993.65	7.67	26.04
C2-O	$P-1$	1.90	4972.09	7.90	28.58
C3-O	$P2_12_12_1$	1.97	7162.56	9.14	39.08
D1	$P-1$	1.76	5416.25	7.37	23.79
D2	$Pna2_1$	1.94	4318.97	7.75	27.81
D3	$P2_1$	2.05	6777.53	9.29	41.25
D1-O	$P2_1$	1.85	6152.87	8.05	29.26
D2-O	$P-1$	1.93	5035.71	8.14	30.66
D3-O	$P-1$	2.00	7290.72	9.38	41.48
RDX[a]		1.82	5622.50	8.75	34.00
HMX[a]		1.91	5629.86	9.10	39.00

[a] Experimental values from ref. [68]
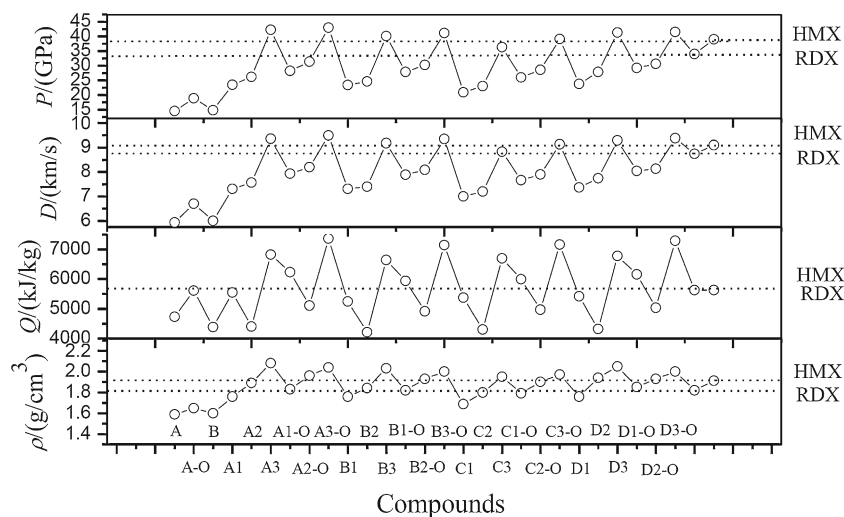
BO is a theoretical index of the degree of bonding between two atoms. It can be used as a measure of the bond strength [49, 69]. From Table 4 it can be seen that the BO of the ring-NO_2 bonds are smaller than those of the C-X (X= -NH-, -CH_2-, -O-) bonds except for some -NH_2 derivatives, such as A2, A2-O, C2, D2, D2-O, in which the BO of ring-NO_2 bonds are slightly bigger than those of the C-X bonds. These indicate that the trigger linkage in most of these dipyridines appears to be the ring-NO_2 bonds, which are easier to break than other bonds according to the principle of the smallest bond order (PSBO) [70]. For A2, A2-O, C2, D2, and D2-O, the decomposition process is possibly initialized from the breaking of the bridge C-N, C-C, or C-O bonds.

The BDE of the trigger bond is often a key factor in investigating the stability and pyrolysis mechanism for energetic compounds [71–74]. Generally, the less the energy is needed for breaking a bond, the weaker the bond is, and the easier the molecule is broken [28, 39, 42]. To elucidate the pyrolysis mechanism and thermal stability of the title compounds, the BDEs of the weak bonds (ring-NO_2 or C-X) were calculated and the results are also listed in Table 4. For all compounds except D2-O, the BDE of ring-NO_2 bond is much smaller than that of the C-X bond, which shows that the ring-NO_2 bond may be the trigger bond during the thermolysis initiation process. Figure 3 plots the BDE of the weakest bonds for various bipyridines. We see that the BDEs of all compounds are in the range of 200~300 kJ mol^{-1}. The bridge group of bipyridine has little effect on the BDE value. We can also see from Fig. 3 that the BDE values are in the order of series 2 > series 1 > series 3, which is also the order of the relative thermal stability of the title compounds. This indicates that the amino group is helpful for improving stability, but the nitro group lowers stability. What's more, in series 2, all amino and nitro groups are

Fig. 2 Densities, heats of detonation, detonation velocities, and detonation pressure of the title compounds

Table 4 Calculated bond order (BO), bond dissociation energies (BDE, kJ mol^{-1}), and characteristic height (h_{50}, cm)[a]

Compounds	BO		BDE		h_{50}
	Ring-NO$_2$	C-X[b]	Ring-NO$_2$	C-X[b]	
A1	0.9260	0.9697	254.30	411.20	48
A2	1.0176	0.9688	294.25	389.47	53
A3	0.8734	1.0021	207.38	414.20	6
A1-O	0.9138	1.0211	242.50	506.10	39
A2-O	1.0167	0.9916	292.53	478.32	54
A3-O	0.8878	1.0110	211.17	495.02	4
B1	0.9195	1.0929	232.55	399.91	50
B2	1.0566	1.0931	308.85	397.33	56
B3	0.8692	1.0704	206.43	390.16	8
B1-O	0.9273	1.1484	267.42	379.45	41
B2-O	1.0282	1.1435	279.92	351.02	55
B3-O	0.8742	1.1272	202.07	374.38	6
C1	0.9270	1.0037	261.92	333.43	51
C2	1.0236	0.9966	288.55	328.44	55
C3	0.8614	1.0016	207.72	333.30	8
C1-O	0.9094	1.0119	245.52	349.42	45
C2-O	0.9925	1.0064	269.08	336.72	56
C3-O	0.8797	1.0078	225.76	345.99	6
D1	0.9276	0.9344	252.06	339.08	47
D2	0.9903	0.9358	281.27	319.48	53
D3	0.8694	0.9659	207.30	323.33	5
D1-O	0.9192	0.9955	247.42	268.33	41
D2-O	0.9991	0.9967	273.41	235.91	55
D3-O	0.8908	0.9869	206.76	260.94	4
RDX			153.80		29(28)[a]
HMX			166.50		33(32)[a]

[a] Data in the parentheses are the experimental values taken from Ref. [76]

[b] X=NH, CH$_2$, O

Fig. 3 Bond dissociation energies (BDE) and the characteristic height (h_{50}) of the title compounds
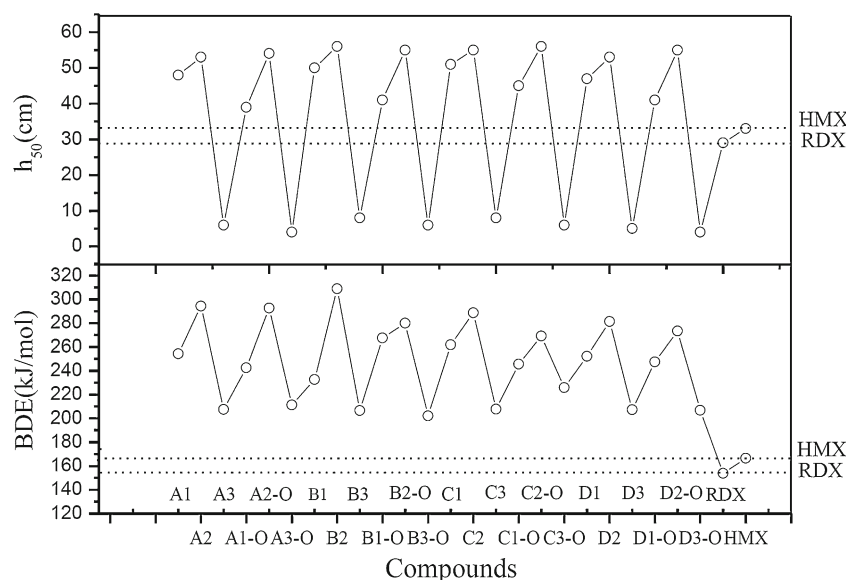
suited at the adjacent positions, so they can form hydrogen bonds to further stabilize the compounds.

The characteristic height h_{50} predicted in this study is also shown in Fig. 3. The predicted h_{50} values have the order of series 2 > series 1 > series 3 too. Since the greater h_{50} a compound has, the less sensitive the compound is [65], therefore -NO$_2$ group increases while -NH$_2$ group lowers the impact sensitivity, which also confirms that the amino group has an insensitizing effect. It is in harmonic agreement with the conclusion from BDE.

However, the conclusion from h_{50} is not always consistent with that from BDE. For the pyridines studied in this work, the BDE values of the weakest bonds are all above 200 kJ mol^{-1}, much higher than that of RDX (153.80 kJ mol^{-1}) and HMX (166.50 kJ mol^{-1}). It seems that all pyridines are much more stable and less sensitive than RDX and HMX to thermal and impact stimuli according to the results of BDE. However, the h_{50} of A3, A3-O, B3, B3-O, C3, C3-O, D3, and D3-O is smaller than that of RDX and HMX, which supports the proposed of Politzer [75] that the correlation between bond strength and impact sensitivity is not general but limited within certain classes of molecules. To test the reliability of the predicted h_{50} and BDE, further calculations were performed on 1,3,5-Trinitrobenzene, 1,2,3,5-Tetranitrobenzene, and Hexanitrobenzene (HNB), and the results of BDEs (267.84, 210.49, and 209.79 kJ mol^{-1}) and h_{50}s (45, 25, and 6 cm, respectively), are in reasonable agreement with the experimental h_{50}s (71, 28, and 11 cm) [76]. Though the order of the stability of three compounds predicted by BDE and h_{50} are the same, the result for individual compound from BDE is unrealiable. For example, according to the experimental and calculated h_{50}, HNB is sensitive because of large repulsion caused by many adjacent nitro groups. However, the value of BDE indicates it is stable. Obviously, h_{50} is more reliable than

BDE for predicting stability here. Though A3, A3-O, B3, B3-O, C3-O, D3, and D3-O have good detonation performance over RDX and HMX, but their h_{50} is very low. A2-O, B2-O, C2-O, and D2-O, which have close detonation performance with RDX, have quite big h_{50} and are more stable than RDX and HMX. They are worth further consideration.

Conclusions

In this work, the properties of a set of bipyridines with different linkages and energetic substituent groups have been studied theoretically. The gas-phase HOFs are predicted with isodesmic reactions and the condensed-phase HOFs are estimated in the framework of the Politzer approach. The results show that all compounds except the -NH$_2$ derivatives posses large HOFs and incorporating the -CH$_2$-, -NH-, or -O- bridge into dipyridines is unfavorable for increasing HOF but the oxidation of the pyridine N improves HOF. The crystal density has been computed through molecular packing calculations. All compounds have quite large density (1.69~2.08 g/cm^3). Incorporating -NH- and -O- into dipyridines is helpful for increasing density, but it is not the case for -CH$_2$-.

The calculated detonation velocities and detonation pressures indicate that both -NH$_2$ and -NO$_2$ can enhance the detonation properties with the latter being more prefered. The N-oxidation of pyridine derivatives can also improve the detonation properties. Linking pyridines with -O-, -NH-, or -CH$_2$- bridge groups can not improve the detonation properities in comparison with the directly linked bipyridines. The sensitivity judged from h_{50} may be more reliable than that from BDE. An analysis of the bond dissociation energies or the impact sensitivity suggests various bridged bipyridines with the same substituents have little difference in their thermal stability. The amino group is helpful for improving stability, but the nitro group lowers stability.

Considering the detonation performance and stability, A2-O, B2-O, C2-O, and D2-O that have similar detonation performance with and lower sensitivity than RDX may be worth further investigations.

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