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Study on the Tetrazine's C-N Heterocyclic Derivatives*)

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Abstract: 31 tetrazine's C-N heterocyclic derivatives have been investigated by density functional theory. Their optimized geometry structures, electronic structures, conjugation, molecular total energies and heats of formation (HOF) were calculated at the B3LYP/6-311G(d,p) level. The results show that most of the species keep a planar structure and exist considerable conjugation over the whole molecule, which enhances the stability of these derivatives. There are good linear relationships among the molecular total energy, HOF and N atoms in these species. Our study shows most of the species have high HOFs and relative stabilities. The HOFs of these compounds are between 571.2KJ/mol and 827.2KJ/mol, so they may be potential candidates for energetic materials.

Keywords: tetrazine, C-N heterocycle, theoretical study, heat of formation

Introduction

Energetic materials are used extensively both for civil and military applications. In order to meet the requirements of future military and space applications, there are continuous researches on how to develop new energetic

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materials with higher explosive performance and enhanced insensitivity to thermal or shock insults than the existing ones. In the past, high explosive performance has always been a prime requirement in the field of research of explosives, so the traditional explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-etrazocine (HMX) were considered adequate for all weapon applications. But in modern ordnance, because many catastrophic explosions results from unintentional initiation of munition by either impact or shock, aboard ships, aircraft carriers, and munition trains. The explosives with the good thermal stability, impact and shock insensitivity, and better performance are strongly required. However, these demands are somewhat mutually exclusive. The explosives with good thermal stability and impact insensitivity usually exhibit poor explosive performance and vice versa. Therefore, the foremost objective at the stage of synthesis of new explosives is to find the molecule with both good energy capability and optimal safety (reduced vulnerability, shock and impact insensitivity) to those in current use [1].

Modern high-energy-density materials (HEDM) derive most of their energies either (i) from oxidation of the carbon backbone, as with traditional energetic materials [2, 3] or (ii) from their very high positive heat of formation. Examples for the first class are traditional explosives such as TNT, RDX and HMX [4]. Modern nitro compounds such as CL-20 or the recently reported hepta- and octanitrocubanes [5] possess very high densities and have enhanced energies due to substantial cage strain. And the second class of compounds is the high-nitrogen energetic materials, which derive most of their energy from their very high positive heats of formation [6]. In recent years, high-nitrogen energetic organic compounds have attracted great attentions because of their novel properties, such as high density, high positive heat of formation and high thermal stability. The large positive heats of formation of nitrogen-rich compounds make them promising targets for the synthesis of highly energetic materials, as illustrated by the recent examples of 3,3'-azobis (6-amino-1,2,4,5-tetrazine) and hydrazinium *N,N'*-azobis tetrazolate [7]. Among the synthesized high-nitrogen C-N compounds, the tetrazine derivatives are one kind of potential and luminous candidates for high performance insensitive explosive. However, there are few theoretical studies on the tetrazine derivatives.

To help find new stable nitrogen-rich compounds and obtain a more comprehensive picture of the stability of such high-energy compounds, in this paper we studied the structure and stability of a large number of substituted tetrazine compounds by density functional theory (DFT).

Computational details

Theoretical calculations were performed to investigate 31 substituted tetrazine compounds by density functional theory (DFT) [8] with hybrid B3LYP function [9, 10]. The 6-311G(d,p) basis set was used for all geometry optimizations. The self-consistent field (SCF) convergence criterion is set to 10^{-8}. The harmonic vibrational frequencies were calculated to obtain the zero point energies (ZPE). There are no imaginary frequencies for all of the structures at this theoretical level, which suggests that all of the structures that we obtained are the structures of local minima on the potential energy surface (PES). The natural bond orbital (NBO) [11-14] analysis has been performed at the B3LYP/6-311G(d,p) level on the basis of the optimized geometries. All these calculations were carried out using the Gaussian 98 program [15].

Results and Discussion

Single five and six-membered C-N heterocyclic compounds

Firstly, we optimized geometries of tetrazine and triazine with different base sets to find a suitable basis set. And the results were compared with the experimental data, which were illustrated in Table 1. The calculated bond lengths with the 6-311G(d,p) base set is close to experimental values, and the calculation is relatively inexpensive. Thus, we use 6-311G(d,p) basis set for all the five and six-membered C-N heterocyclic compounds.

The results show that all the molecules have a rigid plane structures, and bond lengths of these single rings have an averaged tend. And the average trend of bond lengths for triazine is the most obvious, of which all bond lengths are 1.334 Å. In addition, the stabilization interaction energies E(2), are calculated by means of the second-order perturbation theory. In the NBO analysis, E(2) is used to describe the delocalization trend of electrons from the donor bond to the acceptor bond. Through the analyses, we find that there exist strong donor-acceptor interactions within all the single rings. Interaction energies E(2) (159.95 kJ/mol) between π bonding orbital and π^* antibonding orbital in the triazine ring is the maximum within all the systems. For the tetrazine interaction energies E(2) (102.55 kJ/mol) between π bonding orbital and π^* antibonding orbital shows that the tetrazine also exist strong donor-acceptor interactions. Through molecular orbital analysis, we find a delocalized π occupied orbital composed purely of $2P_Z$ orbitals of all carbon and nitrogen atoms of the ring in all derivatives.

Table 1. The experimental data and theoretical data of 1,2,4,5-tetrazine and 1,3,5-triazine /(Å)

	1,2,4,5-tetrazine		1,3,5-triazine
B3LYP	N—N	C—N	C—N
6-311G(d,p)	1.322	1.336	1.334
6-311G++(d,p)	1.321	1.336	1.334
cc-pvdz	1.324	1.340	1.338
cc-pvtz	1.318	1.333	1.331
aug-cc-pvdz	1.323	1.340	1.338
aug-cc-pvtz	1.317	1.333	1.331
Experiment [16]	1.321	1.334	1.338

Substitute of the single ring

Geometry analyses

As some investigations showed, many organic molecules exhibit much different property when its group substituted. At present many known high-nitrogen energetic materials take the tetrazine as the parent structure because of its better conjugation and high-nitrogen content. So we discuss the structures and the electronic structures of these derivatives coming from C-N heterocycle directly substitute a hydrogen atom of the tetrazine, and we gained the thirty-one molecules aggregately. At first, we optimize the geometry of all the molecules at the B3LYP/6-311G(d,p) level and the results see the Figure 2 and 3. As shown in the two Figures, two rings of the molecules T2j-a, T2l-a, T3, TT and T42-1 are not in a plane, their dihedral angels are 37.3°, 16.8°, 41.2° and 24.9°, and the other molecules have a plane structure. We fixed two rings of these non-plane molecules at a plane, then optimize their structures, at last we find a imaginary frequency and higher molecular energy. The results show that the non-plane structure of these molecules is the most stable.

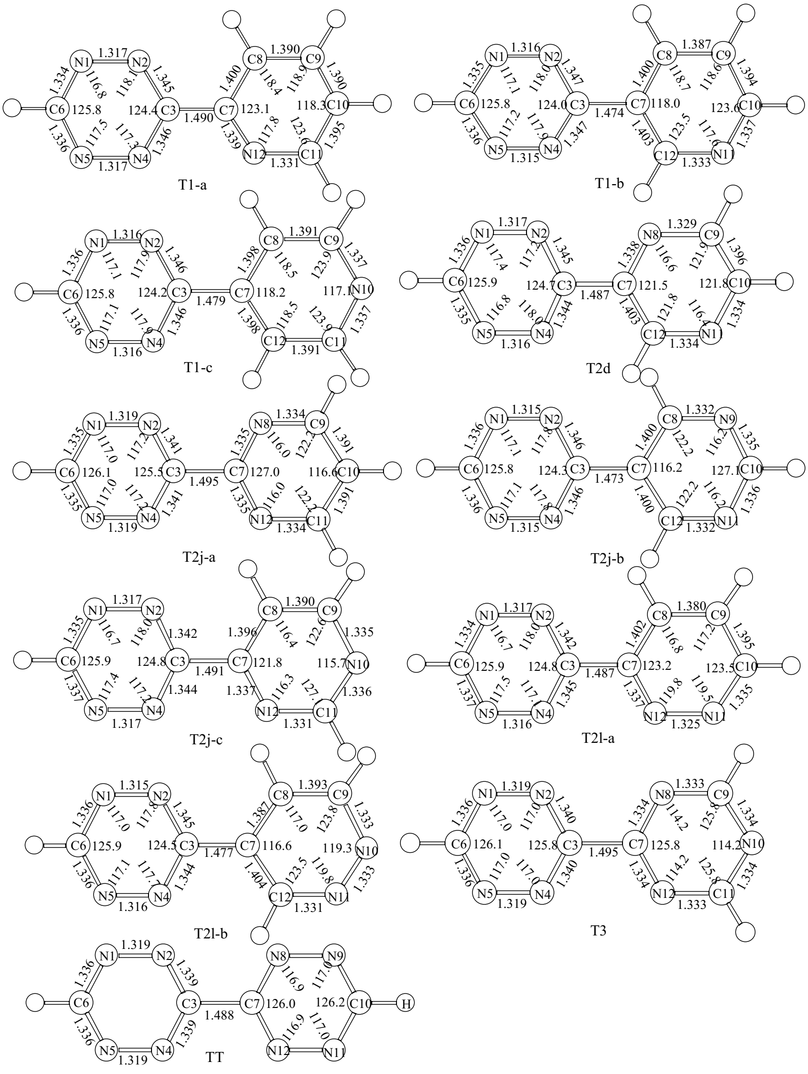

Figure 1. The molecular structures and parameters of the tetrazine substituted by six-membered C-N heterocycle.

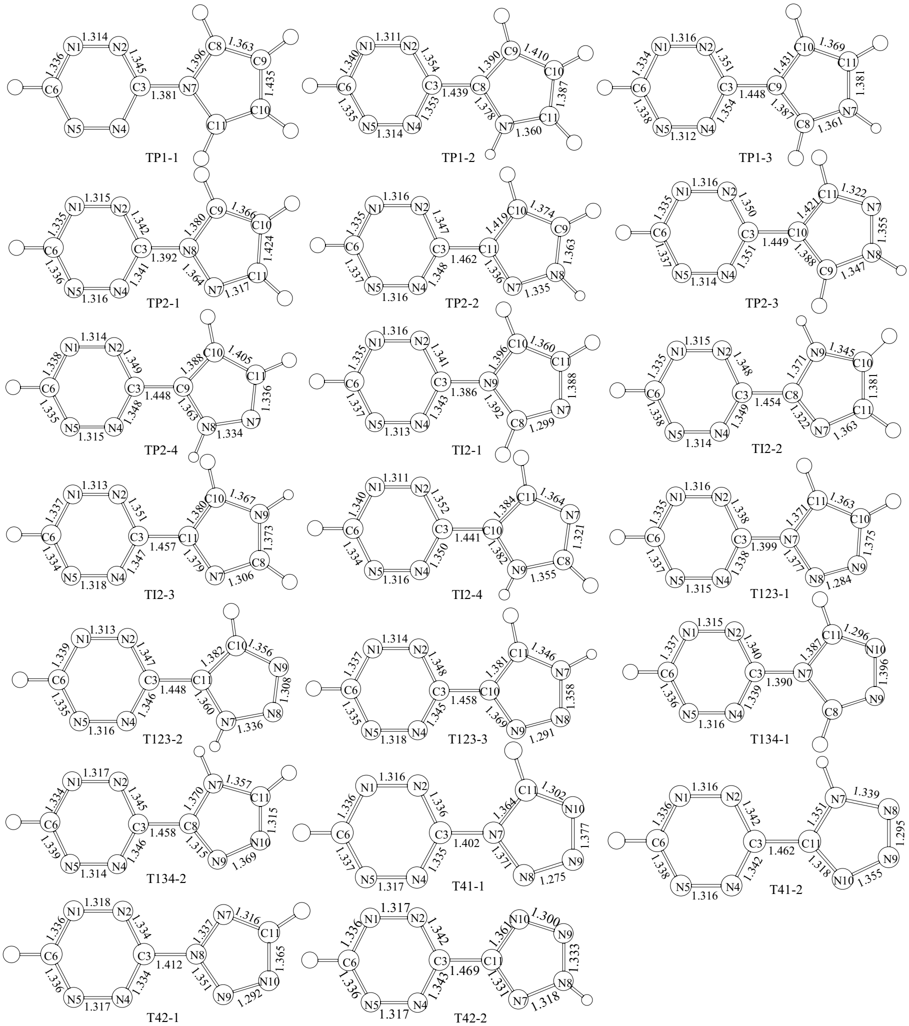

Figure 2 The molecular structures and parameters of the tetrazine substituted by five-membered C-N heterocycle.

From the two Figures, we can know that after a hydrogen atom of the tetrazine is substituted, the NN bond lengths become shorter, the CN bond lengths adjacent to the substituent become longer and the CN bond lengths far from them have no change basically. From the Figure 1, we can find that for the same substituent the different place connected with the tetrazine has a different influence on the C3-C7 bond length between the two rings, such as these molecules T2j-a, T3-a and TT, their C3-C7 bond lengths are 1.495 Å, 1.495 Å and 1.488Å, which are more than that of T1-a, T2d, T2j-c and T2l-a, because a hydrogen atom of the substituent is closer to one nitrogen atom of the tetrazine in the latter; the other molecules have two hydrogen atoms closer to the nitrogen atoms of the tetrazine, their C3-C7 bond lengths are the shortest correspondingly. This trend is more obvious in the isomers T2j-a,b,c. The distance between the hydrogen and the nitrogen of tetrazine ring is between 2.447 Å~2.531 Å, there maybe exist the weak interaction, but there are no the bond critical point between the two atoms from the results of AIM analyses, namely there don't form the hydrogen bonding. As Figure 2 shows, the C-N bonds of the subsituent connected the tetrazine in the molecules TP1-1, TP2-1, TI2-1, T123-1, T134-1, T41-1and T42-1 are close to 1.40 Å, the shortest is 1.381 Å and the longest is 1.412 Å; the C-C bonds of the other molecules are more than 1.40 Å (between 1.439 Å~1.469 Å). In a word, these bonds are between the standard single bond and double bond.

Electronic structures and conjugation

The net charge of all the atoms is calculated by the NBO method. A hydrogen atom of the tetrazine ring is taken as a substituent and the C-N heterocycle is taken as a whole, the total charge of all the substituents are calculated. Table 2 illustrates the NBO charge of C3 atom of tetrazine rings and the total charge of the tetrazine ring and the subsitituent.

As shown in Table 2, after the C-N heterocycle substitutes a hydrogen atom connected with the atom C3 of the tetrazine, the positive charge of C3 atom increases obviously. A part of electrons on the tetrazine rings shift to the substituent. It indicates that the C-N heterocycle as the substituent has an electron-absorbing characteristic. The electron-absorbing characteristic of the six-membered C-N heterocyclic substituent would boost up along with the increase on the number of nitrogen atom. And the electron-absorbing characteristic of the five-membered C-N heterocyclic substituent is related to not only the number of nitrogen atom, but also the place of the C-N heterocycle connected with the tetrazine. When the nitrogen atom of the C-N heterocycle connected with the tetrazine ring, the electron-absorbing characteristic is stronger than the others connecting with the carbon atom. As above discussed, the electron-absorbing characteristic of the substituent 2H-tetrazole (42) is strongest among all the whole system.

Table 2. The atom's NBO charge distribution of the tetrazine ring and the total charge of two rings/(a.u.)

	C3	Total charge of the tetrazine rings	Total charge of the substituents
T	0.215	-0.196	0.194
T1-a	0.355	-0.054	0.055
T1-b	0.372	-0.063	0.063
T1-c	0.370	-0.046	0.048
T2d	0.348	-0.043	0.044
T2j-a	0.342	-0.031	0.030
T2j-b	0.367	-0.049	0.050
T2j-c	0.347	-0.029	0.029
T2l-a	0.352	-0.036	0.035
T2l-b	0.364	-0.034	0.033
T3	0.332	-0.012	0.010
TT	0.329	-0.001	-0.001
TP1-1	0.559	0.074	-0.074
TP1-2	0.341	-0.151	0.150
TP1-3	0.371	-0.115	0.115
TP2-1	0.546	0.112	-0.110
TP2-2	0.353	-0.074	0.073
TP2-3	0.368	-0.093	0.095
TP2-4	0.345	-0.095	0.094
TI2-1	0.555	0.102	-0.102
TI2-2	0.329	-0.105	0.104
TI2-3	0.352	-0.091	0.091
TI2-4	0.342	-0.123	0.123
T123-1	0.542	0.142	-0.143
T123-2	0.342	-0.071	0.071
T123-3	0.349	-0.064	0.066
T134-1	0.552	0.127	-0.129
T134-2	0.329	-0.067	0.068
T41-1	0.537	0.165	-0.165
T41-2	0.325	-0.029	0.029
T42-1	0.525	0.187	-0.187
T42-2	0.325	-0.028	0.027

Table 3. The part stabilization interaction energies E(2) of the tetrazine substituted by five-membered C-N heterocycle/(KJ/mol)

	Donor	Acceptor	E(2)
T1-a	LP C3	BD* N1-N2	511.45
	LP C3	BD* N4-N5	458.61
	LP C3	BD* C7-C8	136.69
T1-b	BD C7-C12	BD* N2-C3	103.72
T1-c	LP C6	BD* N1-N2	472.33
	LP C6	BD* N4-N5	472.33
	BD C7-C8	LP* C3	217.82
T2j-a	LP C3	BD* N1-N2	489.36
	LP C3	BD* N4-N5	489.32
	LP C3	BD* C7-N8	121.17
T2j-b	BD C7-C12	BD* C3-N4	91.55
T2j-c	LP C3	BD* N1-N2	504.09
	LP C3	BD* N5-N4	455.55
	LP C3	BD* C7-C8	140.62
T2l-a	BD C7-N12	BD* N2-C3	58.20
T2l-b	BD C7-C8	BD* C3-N4	90.33
T2d	LP C3	BD* N4-N5	495.01
	LP C3	BD* N1-N2	452.25
	LP C3	BD* C7-C12	133.51
TP1-1	LP N7	BD* C3-N4	234.72
TP2-1	LP N8	BD* N2-C3	204.89
TI2-1	LP N9	BD*N2-C3	221.54
T123-1	LP N7	BD* N2-C3	190.83
T134-1	LP N7	BD* N2-C3	208.11
T41-1	LP N9	BD* N2-C3	179.45
T42-1	LP N8	BD* N2-C3	135.90

In order to study the interaction between the substituent and the tetrazine ring, the stabilization interaction energies E(2) are calculated by means of the second-order perturbation theory. The selected stabilization interaction energies E(2) for all the molecules at the B3LYP/6-311G(d,p) level are summarized in Table 3, where BD and BD* represent bonding and antibonding natural bond orbital and LP represents lone pairs. From the Table 3, we find that the interaction between the lone pairs of C atom and π^* antibonding orbitals of the tetrazine ring becomes strong for the molecules including six-membered C-N heterocycle, E(2) values are more than 100 Kcal/mol. And in the other systems, interaction between the bonding and antibonding orbital has no change basically. Except for T3 and TT (their values are not included in Table 3), the others exist strong interaction between the two rings. In addition, the results of NBO analyses show that when the nitrogen atom of five-membered C-N heterocycle connected the tetrazine ring, there exit strong donor-acceptor interaction between the LP of N atom in the C-N heterocycle and the CN π^* antibonding orbitals in the tetrazine ring.

In addition, from the analyses of molecular orbitals, we get much conjugate information about the molecules of the tetrazine substituted by the single ring, Figure 3 shows the delocalized π occupied orbital in all the molecules. The Figure shows that there exists a delocalized π occupied orbital composed of purely $2P_Z$ orbital of all carbon and nitrogen atoms in the molecules T3,TT and the isomers TP2, TI2, T123, T134, T41 and T42. Although other molecules have no π orbital over the whole molecule, interaction between the two rings do not destroy the primary conjugation of the tetrazine ring, and the conjugate orbital expands its range to some atoms of the substituent. As above analyzed, after a hydrogen atom of the tetrazine is substituted by the C-N heterocycle, there exists strong interaction between the two rings. This interaction do not destroy the delocalized π orbital of the tetrazine, and in some cases it can form a delocalized π occupied orbital over the whole molecule. This delocalized π orbital is advantage to the stabilization of the whole molecule.

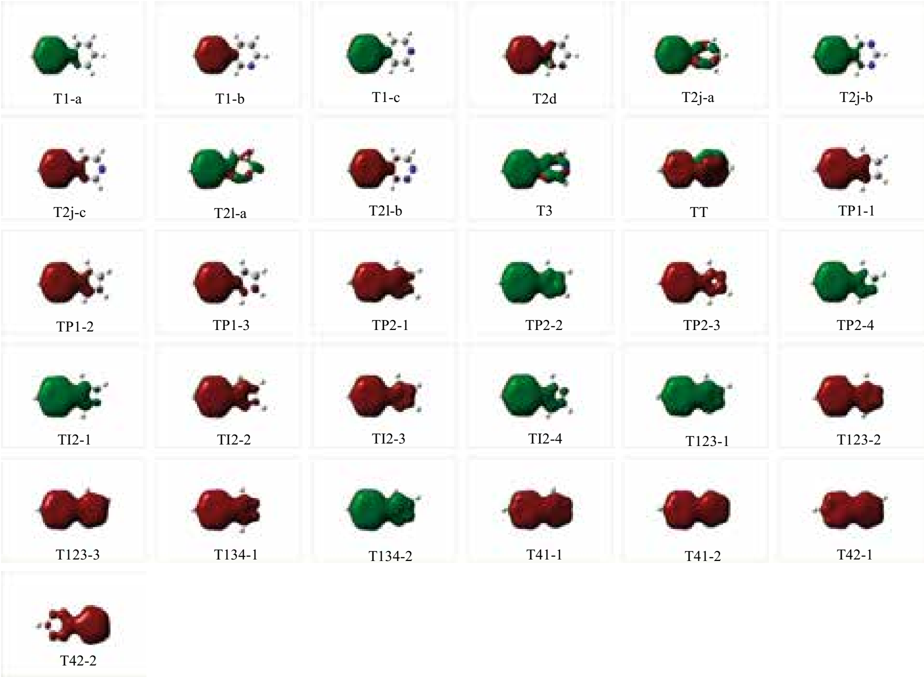

Figure 3. The delocalized π occupied orbitals of the tetrazine substituted by the C-N heterocycle.

Molecular Total Energy (E_{total}) and Heat of Formation (HOF)

Energy analysis

As shown in Table 5, with the increase of the nitrogen atoms in the C-N heterocyclic substituent, the molecular total energy decreased gradually. The isomer with the minimum energy is considered as the steadiest structure. Figure 4 shows the relation of (E_{total}) and nitrogen atom numbers. The results show that the molecular total energy will decrease gradually with the increase of the nitrogen atoms, and it submitted good linearity relation. The molecular total energy (E_{total}) decreased about 16 a.u when increasing a nitrogen atom.

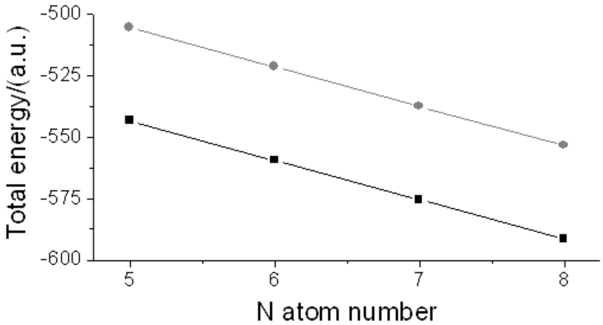

Figure 4. The relationship between the molecular total energy and N atom number for C-N compounds.

Heat of formation analyses

Heat of formation is a critical parameter of energetic materials and the calculation of the velocity of detonation. It is a key to design and synthesize new energy materials. And high-nitrogen energetic materials possess very high positive heat of formation, which attracts many researchers' attention. So the calculation of HOF is a significant matter for theoretical study and experimental study. In this paper, HOF of the objective compounds are calculated through atomic scheme. The different methods were adopted to calculate the academic values of HOF for the single six-membered C-N heterocycle, and these results are compared with the experimental data, which are illustrated in Table 4. The point energy is calculated at the B3LYP/6-311+G(2df,2p) level, then it is corrected by the ZPE which is calculated at the B3LYP/6-311G(d,p) level. Finally we take corrected molecular energy as a parameter to calculate heat of formation; the results are in the last column of Table 4. From the data of Table 4, we find that the results of this method show a good agreement with the experimental data, and the most error is 19.4 KJ/mol. So we calculated the heat of formation for all the molecules using the above method discussed. The results are in Table 5.

Table 4. The experimental data and theoretical data of HOF for the single six-membered C-N heterocycle/(KJ/mol)

Compounds	Experimental data[16]	G3	B3LYP		
			6-311G(d,p)	6-311 +G(2df,2p)	6-311 +G(2df,2p) (ZPE correction)
(1) pyridine	144.77	143.0	184.3	155.1	145.8
(2d) pyradine	196.23	209.0	237.5	204.2	196.2
(2j) pyrimidine	196.65	190.3	220.4	187.6	179.5
(2l) pyridazine	278.24	285.3	313.7	280.2	272.2
(3) 1,3,5-triazine	225.52	229.0	249.5	213.0	206.1
(T) 1,2,4,5-tetrazine	464	489.7	496.8	455.5	450.1

Table 5. The molecular energy and HOF of all the compounds

	Energy (a.u.)	$\Delta_f H^{\circ}$(298K) (KJ/mol)
T1-a	-543.5430	639.1
T1-b	-543.5466	631.1
T1-c	-543.5458	632.5
T2d	-559.5758	692.4
T2j-a	-559.5787	683.5
T2j-b	-559.5864	667.8
T2j-c	-559.5823	676.4
T2l-a	-559.5454	769.9
T2l-b	-559.5492	761.7
T3	-575.6211	712.9
TT	-591.5778	960.1
TP1-1	-505.4232	606.8
TP1-2	-505.4371	571.2
TP1-3	-505.4336	580.2

	Energy (a.u.)	$\Delta_f H^{\circ}$(298K) (KJ/mol)
TP2-1	-521.4500	677.1
TP2-2	-521.4595	653.2
TP2-3	-521.4647	641.2
TP2-4	-521.4644	641.4
TI2-1	-521.4700	625.6
TI2-2	-521.4799	599.8
TI2-3	-521.4787	602.4
TI2-4	-521.4842	588.9
T123-1	-537.4709	759.8
T123-2	-537.4870	720.1
T123-3	-537.4840	727.7
T134-1	-537.4925	705.9
T134-2	-537.5013	682.5
T41-1	-553.4995	825.0
T41-2	-553.5110	796.0
T42-1	-553.4993	827.2
T42-2	-553.5115	797.2

The results (Table 4) show that the different type of bond has different contributions to HOF, the sequence is NN bonds>CN bonds>CC bonds. For example, the tetrazine (T) has two NN bonds, the pyridazine(2l) has a NN bond, and the triazine(3) has no NN bond, so HOF of tetrazine> HOF of pyridazine> HOF of triazine. And the triazine has three CN bonds, the pyriazine(2d) or the pyrimidine(2j) has two CN bonds and the pyridine(1) has only one CN bond, so HOF of triazine> HOF of pyriazine or pyrimidine> HOF of pyridine. When C-N heterocycle as the substituent (see Table 5), the system follow the same rule. For example, the number of NN bonds in the tetrazole is the most, so its HOF is the most one among all the molecules. In addition, when two rings are connected with the CN bond, its HOF is more than that of those molecules which two rings are connected with the CC bond.

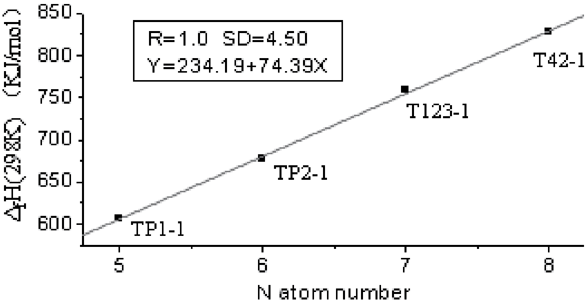

Figure 5. The relationship between the HOF and the number of N atoms.

We take out the HOF of TP1-1, TP2-1, T123-1 and T42-1 (because their HOFs are the maximum in the isomers) and analyze the relationship between the HOF and the number of N atom in these molecules, (see Figure 5) This curve has a good relativity. The Figure 5 shows that the HOF would boost up linearly along with the increase of the nitrogen atom's number when five- membered heterocycle connected the tetrazine ring with CN bond.

Conclusions

In this paper, after a hydrogen atom of the tetrazine is substituted by the C-N heterocycle, we obtain 31 tetrazine's C-N heterocyclic derivatives and their optimized geometries, electronic structures, conjugations, energies, and heats of formation have been investigated by the DFT methods. The results show: (1) When the nitrogen heterocycle replaces a hydrogen atom on tetrazine, NN bonds on tetrazine rings are shorter and CN bonds which are close to the substituent are longer, the other bonds change little. (2) In these derivatives, the conjugations of the tetrazine rings are not destroyed. The part system forms a delocalized π occupied orbitals composed by $2P_Z$ orbitals of all atoms, which enhances the stability of the molecule. (3) The C-N heterocycles as the substituent have a strong absorbing-electron characteristic, and the five- memebered ring 42 (2H-tetrazole) among them has the strongest absorbing-electron characteristic. (4) There are a good linear relationship between the energies, HOFs and the number of N atoms, the total molecule energy decrease about 16 a.u when increasing a nitrogen atom. The HOFs would boost up linearly along with the increase on the number of nitrogen atom when five-membered heterocycle connected the tetrazine ring with CN bond. Our study shows that most of the species have high HOFs and relative stabilities. The HOFs of these compounds are between 571.2 KJ/mol and 827.2 KJ/mol, so they may be potential candidates for energetic materials.

References

[1] Sikder A. K., Sikder, A Review of Advanced High Performance, Insensitive and Thermally Stable Energetic Materials Emerging for Military and Space Applications, *J. Hazard. Mater.,* **2004**, *A112*(1-2), 1-15.

[2] Feuer H., Nielsen A. T., *Nitro Compounds;* VCH, NewYork, Weinheim, Cambridge **1990**.

[3] Nielsen A. T., *Nitrocarbons,* VCH, New York, Weinheim, Cambridge **1995**.

[4] Köhler J., Meyer R., *Explosivstoffe,* 7th ed., Wiley-VCH, Weinheim **1991**.

[5] Zhang M.-X., Eaton P. E., Gilardi R., Hepta- and Octanitrocubanes, *Chem. Int. Ed.,* **2000**, *39*(2), 401-404.

[6] Hammerl Anton, Klapötke Thomas M., Schwerdtfeger P., Azolylpentazoles as High-Energy Materials: A Computational Study, *Chem. Eur. J.,* **2003**, *9,* 5511-5519.

[7] Hammerl A., Klapötke T. M., Nöth H. et al., Synthesis, Structure, Molecular Orbital and Valence Bond Calculations for Tetrazole Azide, CHN_7, *Propellants, Explos., Pyrotech.,* **2003**, *28*(4), 165-173.

[8] Parr R. G., Yang W., *Density-functional Theory of Atoms and Molecules;* Oxford University Press, New York 1989.

[9] Becke A. D., Density-functional Thermochemistry. III. The Role of Exact Exchange, *J. Chem. Phys.,* **1993**, *98*, 5648.

[10] Lee C., Yang W., Parr R. G., Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density, *Phys. ReV. B.,* **1988,** *37*(2), 785-789.

[11] Carpenter J. E., Weinhold F., Analysis of the Geometry of the Hydroxymethyl Radical by the "Different Hybrids for Different Spins" Natural Bond Orbital Procedure, *J. Mol. Struct. (THEOCHEM)*, **1988**, *169,* 41-62.

[12] Reed A. E., Curtiss L. A., Weinhold F., Intermolecular Interactions from a Natural Bond Orbital, Donor-acceptor Viewpoint, *Chem. ReV.,* **1988**, *88*(6), 899-926.

[13] Foster J. P., Weinhold F., Natural Hybrid Orbitals, *J. Am. Chem. Soc.,* **1980**, *102,* 7211-7218.

[14] Reed A. E., Weinstock R. B., Weinhold F., Natural Population Analysis, *J. Chem. Phys.,* **1985**, *83*(2)*,* 735-746.

[15] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Zakrzewski V. G., Montgomery J. A. Jr., Stratmann R. E., Burant J. C., Dapprich S., Millam J. M., Daniels A. D., Kudin K. N., Strain M. C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S.,Ochterski J., Petersson G. A., Ayala P. Y., Cui Q., Morokuma K., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Cioslowski J., Ortiz J. V., Stefanov B. B., Liu G., Liashenko A., Piskorz P., KomaromiI., Gomperts R., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P. m.W., Johnson B., Chen W., Wong M. W., Andres J. L., Gonzalez C., Head-Gordon M., Replogle E. S., Pople J. A., *Gaussian 98 Revision A.11, Gaussian Inc.:* Pittsburgh PA **2001**.

[16] Lias S. G., Libman J. F, Levine R. D., *J. Phys.Chem. Ref. Data.* **1984**, *13,* 695.