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A Density Functional Theory Investigation on the Isomers of Tetrazene

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Abstract: Density functional method was applied to the study of the isomers of the primary explosive of tetrazene. The geometrical structures of the three isomers of tetrazene molecule which had been proposed formerly were fully optimized at the B3LYP/6-311 + G^{**} level of theory. The results show that the total energy of (Ⅲ) is less than that of (Ⅰ) and (Ⅱ), indicating that (Ⅲ) is the most stable structure, which is in agreement with the fact that tetrazene molecules in its crystal adopt structures similar to (Ⅲ). The computational results of the IR vibration of the three isomers show that there is no imaginary frequency, which indicates that all of them are possibly existent structures. The NBO charges of the atoms of the three isomers show that the arrangement of atoms of (Ⅲ) facilitates the charge distribution better than (Ⅰ) and (Ⅱ). It can be concluded from the frontier molecular orbital analysis that N(8) is the most active atom of tetrazene, and bond N(8)—N(12) will break first when it is activated.

Key words: physical chemistry; tetrazene; isomer; molecular structure; density functional theory

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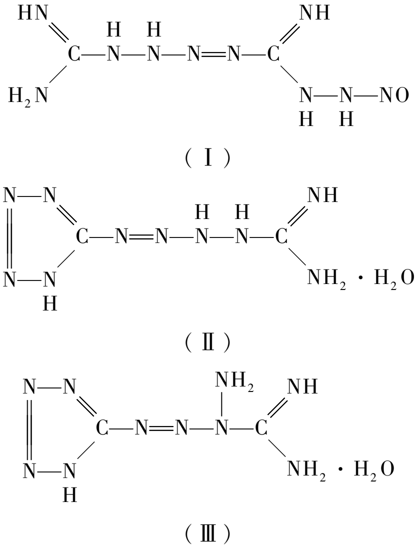
1　Introduction

Tetrazene is a nitrogen-rich primary explosive with right impact and stab sensitivity. It is commonly used as a sensitizer in priming mixtures for varieties of ammunition. Tetrazene was first assigned the structure of (Ⅰ) by Hofmann and co-workers in 1911[1]; the structure of (Ⅱ) was suggested by Patinkin in 1954[2]; the structure of (Ⅲ) has been determined through X-ray crystallographic methods using Cu-radiation data collected with a Hilger and Watts four-circle diffractometer by Duke in 1971[3]. The molecular structures of these three isomers of tetrazene are shown in Scheme 1.

In 1986, the semiempirical MO method was used to calculate the electronic structure of tetrazene by SHENG Di-lun[4]. In 1998, George[5] used semi-empirical quantum mechanic code PM3 to model the tetrazene decomposition. He selected the distance of the broken C(7)—N(6) bond as the reaction coordinate. This is not consistent with the thermal decomposition mechanism of tetrazene of which was proposed by Bird[6]. To the best of our knowledge, there were no theoretical studies on the structures of tetrazene. In this paper, the three isomers of tetrazene (Ⅰ), (Ⅱ) and (Ⅲ) were investigated theoretically in order to testify that (Ⅲ) is the most stable molecular structure. Natural bond orbital (NBO) charge analysis and frequency calculations were also performed on the optimized structures.



Scheme 1

2　Computational methods

The DFT method deals with the electron correlation but is still computationally economic. DFT-B3LYP denotes

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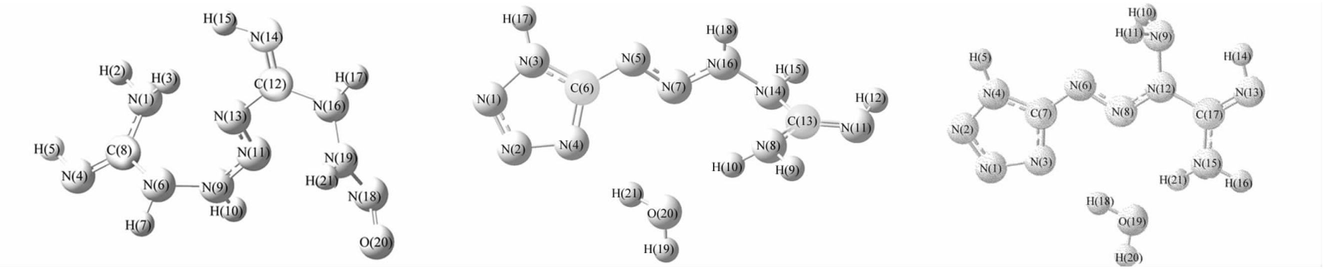
the combination of the Becke's three parameter hybrid function with the Lee-Yang-Parr (LYP) correlation function[7-8]. Because the B3LYP method is more widely used and tested, the hybrid density function of B3LYP with the 6-311 + G** basis set was employed for the calculations. The structures of (Ⅰ), (Ⅱ) and (Ⅲ) were fully optimized and natural bond orbital (NBO) analysis was performed on the optimized structure to obtain reliable atomic charges. The NBO theory applies an interatomic orthogonalization step to establish asymmetrical atomic orbitals[9] and thus gives charges of relatively basis-set independence compared to other methods such as mulliken charges and their variations. All electronic structure calculations were carried out using the GAUSSIAN 98 program package[10].

3 Results and discussion

3.1 Optimized geometries

The fully optimized structures of (Ⅰ), (Ⅱ) and (Ⅲ) were shown in Fig. 1. The optimized geometries of (Ⅲ) are in good agreement with the observed (X-ray) crystal structure of tetrazene[3]. Table 1 lists the optimized geometrical parameters of (Ⅲ).



(Ⅰ)　(Ⅱ)　(Ⅲ)

Fig. 1 The optimized structures and atomic numbering of the three isomers of tetrazene

Table 1 The optimized geometries of structure (Ⅲ) at the B3LYP/6-311 + G** level

bond	bond lengths/Å	bond	bond angles/(°)	bond	dihedral angles/(°)
N(1)—N(2)	1.2877	N(2)—N(1)—N(3)	111.27	N(3)—N(1)—N(2)—N(4)	0.01
N(1)—N(3)	1.3567	N(1)—N(2)—N(4)	106.02	N(2)—N(1)—N(3)—C(7)	0.12
N(2)—N(4)	1.3507	N(1)—N(3)—C(7)	106.35	N(1)—N(2)—N(4)—H(5)	-179.94
N(3)—C(7)	1.3237	N(2)—N(4)—H(5)	121.43	N(1)—N(2)—N(4)—C(7)	-0.12
N(4)—H(5)	1.0093	N(2)—N(4)—C(7)	109.01	N(1)—N(3)—C(7)—N(4)	-0.19
N(4)—C(7)	1.3485	H(5)—N(4)—C(7)	129.55	N(1)—N(3)—C(7)—N(6)	-179.44
N(6)—C(7)	1.3841	C(7)—N(6)—N(8)	111.72	N(2)—N(4)—C(7)—N(3)	0.19
N(6)—N(8)	1.2732	N(3)—C(7)—N(4)	107.34	N(2)—N(4)—C(7)—N(6)	179.55
N(8)—N(12)	1.3082	N(3)—C(7)—N(6)	132.04	H(5)—N(4)—C(7)—N(3)	180.00
N(9)—H(10)	1.0187	N(4)—C(7)—N(6)	120.61	H(5)—N(4)—C(7)—N(6)	-0.64
N(9)—H(11)	1.0189	N(6)—N(8)—N(12)	115.39	N(8)—N(6)—C(7)—N(3)	-5.30
N(9)—N(12)	1.4006	H(10)—N(9)—H(11)	106.97	N(8)—N(6)—C(7)—N(4)	175.52
N(13)—H(14)	1.016	H(10)—N(9)—N(12)	107.98	C(7)—N(6)—N(8)—N(12)	179.04
N(13)—C(17)	1.2714	H(11)—N(9)—N(12)	108.19	N(6)—N(8)—N(12)—N(9)	-1.05
N(15)—H(16)	1.0072	N(8)—N(12)—N(9)	123.46	N(6)—N(8)—N(12)—C(17)	-179.50
N(15)—C(17)	1.3547	N(8)—N(12)—C(17)	118.82	H(10)—N(9)—N(12)—N(8)	-53.54
N(15)—H(21)	1.0185	N(9)—N(12)—C(17)	117.70	H(10)—N(9)—N(12)—C(17)	124.92
N(12)—C(17)	1.4599	H(14)—N(13)—C(17)	110.87	H(11)—N(9)—N(12)—N(8)	61.91
		H(16)—N(15)—C(17)	114.01	H(11)—N(9)—N(12)—C(17)	-119.63
		H(16)—N(15)—H(21)	117.50	N(8)—N(12)—C(17)—N(13)	176.62
		C(17)—N(15)—H(21)	123.98	N(8)—N(12)—C(17)—N(15)	-5.27
		N(12)—C(17)—N(13)	121.57	N(9)—N(12)—C(17)—N(13)	-1.91
		N(12)—C(17)—N(15)	113.86	N(9)—N(12)—C(17)—N(15)	176.19
		N(13)—C(17)—N(15)	124.54	H(14)—N(13)—C(17)—N(12)	0.73
				H(14)—N(13)—C(17)—N(15)	-177.16
				H(16)—N(15)—C(17)—N(12)	172.99
				H(16)—N(15)—C(17)—N(13)	-8.98
				H(21)—N(15)—C(17)—N(12)	17.49
				H(21)—N(15)—C(17)—N(13)	-164.47

Of the three isomers of tetrazene, (Ⅰ) is the only one which has no tetrazolyl group. As can be seen from Fig. 1, the structure of aminotetrazolyl group in (Ⅱ) is similar to the corresponding group in (Ⅲ). The difference between the structures of (Ⅱ) and (Ⅲ) lies in the right part of the molecules. In (Ⅲ), there are hydrogen bond interactions between N(9) and H(14) as well as N(8) and H(21). Whereby, two five-membered cycles N(9)—N(12)—C(17)—N(13)—H(14) and N(8)—N(12)—C(17)—N(15)—H(21) can be formed, which contributes to the stability of the system.

The harmonic frequencies and the infrared intensities of (Ⅰ), (Ⅱ) and (Ⅲ) are predicted at B3LYP/6-311+G** level and there is no imaginary frequency, which indicate that the optimized structures correspond to the minimum point on the intramolecular potential energy surface. It can be said that all the three isomers are possibly existent structures. The predicted frequencies and intensities for (Ⅲ) are listed in Table 2 and the main absorption positions of some functional groups are assigned.

Table 2 A full vibration assignments of (Ⅲ) at the B3LYP/6-311+G level**

frequency /cm^{-1}	intensity /km · mol^{-1}	assignment
588.1	105.50	N—H out-of-plane bending
608.5	43.79	N—H out-of-plane bending
619.6	27.61	N—H out-of-plane bending
691.0	90.96	O—H out-of-plane bending
720.3	19.77	N—H out-of-plane bending
842.0	113.41	N—H out-of-plane bending
916.5	69.69	N—H out-of-plane bending
1235.6	91.71	C—N in-plane bending
1301.2	328.77	C—N in-plane bending
1393.2	303.81	N—H in-plane bending
1446.5	48.23	tetrazole ring skeleton
1484.2	491.66	tetrazole ring skeleton
1564.6	126.39	tetrazole ring skeleton
1631.1	56.19	N—H in-plane bending
1661.5	32.66	N—H in-plane bending
1685.8	58.66	N—H in-plane bending
1744.1	347.68	C═N asymmetrical stretching
3442.9	384.35	N—H symmetrical stretching
3457.2	5.41	N—H symmetrical stretching
3525.5	14.62	N—H asymmetrical stretching
3543.4	41.68	N—H stretching
3558.3	628.72	O—H stretching
3646.8	116.83	N—H stretching
3676.1	72.91	N—H asymmetrical stretching

3.2 NBO charges

The NBO charges of the atoms of (Ⅰ), (Ⅱ) and (Ⅲ) were listed in Table 3. Four N atoms were connected in series for N(6)—N(9)—N(11)—N(13) of (Ⅰ), which doesn't facilitate the charge distribution on these atoms. The NBO charges on N(11) are nearly neutral, while N(6), N(9), and N(13) all bear negative charges. Similar thing happens on N(5)—N(7)—N(16)—N(14) of (Ⅱ), the NBO charges on N(7) are nearly neutral, while the charges on N(5), N(16) and N(14) are all negative. For N(6)—N(8)—N(12)—N(9) of (Ⅲ), N(12) is connected with a less negative atom C(17) which can contribute to the charge distribution of these four N atoms. As can be seen from Table 3, the NBO charges on N(8) and N(12) of (Ⅲ) are nearly neutral, and the charges on N(6) and N(9) are negative. The NBO charges on the atoms of tetrazolyl groups of (Ⅱ) and (Ⅲ) are similar: the charges on N(1) and N(2) of tetrazolyl group are all nearly neutral, while the charges on atoms N(3), C(6) (C7) and N(4) are alternatively positive or negative, in order to get a relatively even charge distribution.

Table 3 NBO charges of the three isomers of tetrazene at the B3LYP/6-311+G level**

(Ⅰ)	charges	(Ⅱ)	charges	(Ⅲ)	charges
N(1)	-0.8332	N(1)	-0.0632	N(1)	-0.0524
N(4)	-0.7462	N(2)	-0.0521	N(2)	-0.0631
N(6)	-0.4927	N(3)	-0.3649	N(3)	-0.3864
C(8)	0.5911	N(4)	-0.3812	N(4)	-0.3637
N(9)	-0.2069	N(5)	-0.3479	N(6)	-0.3734
N(11)	0.0299	C(6)	0.5037	C(7)	0.5046
C(12)	0.5587	N(7)	0.0547	N(8)	0.0357
N(13)	-0.3779	N(8)	-0.8398	N(9)	-0.6397
N(14)	-0.6721	N(11)	-0.7470	N(12)	-0.0905
N(16)	-0.4688	C(13)	0.5895	N(13)	-0.7192
N(18)	0.2318	N(14)	-0.4866	N(15)	-0.8219
N(19)	-0.2524	N(16)	-0.2013	C(17)	0.5913
O(20)	-0.3864	O(20)	-0.9716	O(19)	-0.9734

3.3 Energies

Table 4 gives the total energies (E_{total}), zero-point energies (ZPE) and energies of frontier molecular orbitals (E_{LUMO} and E_{HOMO}) of (Ⅰ), (Ⅱ) and (Ⅲ). The total energy of (Ⅲ) is less than that of (Ⅰ) and (Ⅱ), indicating that (Ⅲ) is the most stable structure, which is in agreement with the experimental fact[3] that tetrazene molecules in its crystal adopt structures similar to (Ⅲ). Zero-point energies have little influence on the relative stability of the three structures.

Table 4 Total energies, zero-point energies and energies of frontier molecular orbitals for the three isomers of tetrazene (in kJ · mol^{-1})

energies	(Ⅰ)	(Ⅱ)	(Ⅲ)
E_{total}	-7729285.66	-7730156.48	-7730241.54
ZPE	1694.69	1694.77	1691.09
E_{LUMO}	-927.05	-1078.17	-1133.86
E_{HOMO}	-2822.53	-2789.10	-2738.47
ΔE	1895.48	1710.92	1604.61

As for the energies of frontier molecular orbital, the E_{LUMO} of (Ⅲ) is the lowest among structure (Ⅰ), (Ⅱ) and (Ⅲ), whereas its E_{HOMO} is the highest one. The ΔE ($\Delta E = \Delta(E_{\text{LUMO}} - E_{\text{HOMO}})$) of (Ⅲ) is the lowest one. This is consistent with the fact that tetrazene is a primary explosive which could detonate and decompose easily.

3.4 Frontier molecular orbitals analysis

It can be seen from Table 5 that the contribution of N(8) atomic orbital to LUMO of (Ⅲ) is 35.3%, and the contribution of N(12) atomic orbital to LUMO of (Ⅲ) is 13.2%. The contribution of N(8) atomic orbital to HOMO of (Ⅲ) is 34.6%, and the contribution of N(12) atomic orbital to HOMO of (Ⅲ) is 46.4%. From this point of view, it can be said that N(8) is the most active atom of (Ⅲ), and bond N(8)—N(12) will break first when (Ⅲ) is activated. This is coincident with the results of research on the fragmentation pathway by using electrospray ionization mass spectrometry (ESI-MS)[11].

4 Conclusions

The structures of three isomers of tetrazene have been optimized and IR vibration analyses have been conducted by applying density functional method. The inexistence of imaginary frequency for these three isomers indicate that the three optimized structures correspond to the minimum point on the intramolecular potential energy surface and they are all possible structures. The total energy of (Ⅲ) is the lowest, indicating that it is the most stable structure, which is in agreement with the experimental fact that tetrazene molecules in its crystal adopt structures similar to (Ⅲ). It can be concluded from the frontier molecular orbitals analysis that bond N(8)—N(12) of (Ⅲ) is the weakest and it will break firstly when tetrazene is activated.

Table 5 Orbital contribution of atoms to HOMO and LUMO of (Ⅲ)

atoms	HOMO/%	LUMO/%	atoms	HOMO/%	LUMO/%
N(1)	0.58	0.15	N(8)	34.63	35.29
N(2)	0.22	3.59	N(9)	2.31	7.98
N(3)	0.87	4.20	N(12)	46.35	13.18
N(4)	0.11	5.66	N(13)	4.47	1.34
N(6)	0.87	20.92	N(15)	5.80	0.40
C(7)	0.13	5.17	C(17)	1.64	1.42

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四氮烯异构体的密度泛函理论研究

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摘要： 采用密度泛函理论对四氮烯起爆药的异构体进行研究。在 B3LYP/6-311+G** 水平下对四氮烯三种异构体分子的几何结构进行全优化计算。计算结果表明，(Ⅲ)的总能量比(Ⅰ)和(Ⅱ)都低，这说明(Ⅲ)是最稳定的分子结构，这与四氮烯的晶体结构和(Ⅲ)非常相近这一事实一致。对三种异构体分子的红外振动计算结果表明，它们的分子中都不存在虚频，由此说明这三种异构体都是可能存在的结构。由三种异构体分子的 NBO 电荷可以看出，(Ⅲ)分子中的原子排列比(Ⅰ)和(Ⅱ)便于分子中电荷的分散。前线轨道分析结果表明：N(8)是(Ⅲ)分子中最活跃的原子，在(Ⅲ)被活化的时候，N(8)—N(12)键先断裂。

关键词： 物理化学；四氮烯；异构体；分子结构；密度泛函理论

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(上接566页)

Measurement and Calculation for SCB Electro-explosion Energy Conversion Features

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Abstract: The changes of current, voltage and light intensity of semiconductor bridge (SCB) with discharge time under capacitor energy supply excitation were conducted. The electro-explosion energy conversion processes and phase changes for SCB were analyzed based from the electric energy input and enthalpy change theoretical calculation. Results show that melting ratio, vaporizing ratio and ionizing-ratio of SCB are 61.1%, 14.5% and 70.3% at 2.18 μs, 3.48 μs, and 17.60 μs respectively when the capacitance is 22 μF and the charging voltage is 45 V.

Key words: applied chemistry; pyrotechnics; semiconductor bridge; plasma; electro-explosive energy conversion

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Theoretical Study on Relationship Between Structures and Properties of Pyrazole Compounds

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Abstract: Structures of pyrazole compounds were constructed and their energetic properties were studied theoretically. For 9 pyrazole compounds, their geometry and electronic structures were analyzed by means of natural bond orbital (NBO) theory; their reactivity was analyzed by electrostatic potential distributions, heats of formation and Bader density were also calculated. After that, detonation velocities and Chapman-Jouguet pressures of these compounds were given by means of VLW equation. Results show that there is some aromaticity in the ring of pyrazole compounds, also there is some linear relationship between total energy, density and the number of amine groups respectively. Calculated detonation velocities of these compounds are more than 8.0 km·s^{-1}, which indicate that these compounds are very good potential energetic materials.

Key words: physical chemistry; energetic materials; theoretical study; derivative of pyrazolo[4,3-c] pyrazole; structure and property; detonation performance