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# Theoretical Study for High Energy Density Compounds from Cyclophosphazene

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## 1. Introduction

The phosphazenes have distinguished ancestry. The reaction between phosphorus pentachloride and ammonia was described by Rose in 1834<sup>[1]</sup>, and in an editorial comment, Liebig<sup>[13]</sup> reported work carried out in conjunction with Wöhler. The major reaction product was phospham and a small quantity of a stable crystalline compound containing nitrogen, phosphorus, and chlorine was obtained. Gerhardt and Laurent established that the empirical composition was  $\text{NPCl}_2$ , and Gladstone and Holmes and Wichelhaus measured the vapor density and deduced the molecular formula,  $\text{N}_3\text{P}_3\text{Cl}_6$ <sup>[2]</sup>.

Phosphorus nitrogen compounds are renowned for their ability to form a variety of ring and cage structures. The most prominent P-N ring systems are phosphazanes, featuring single P-N bond<sup>[3]</sup>, and phosphazenes, having multiple P-N bonds<sup>[4-8]</sup>. The two kinds of systems tend to occur in different ring sizes. The polyphosphazene has been used in medical community widely because its excellent biocompatibility and biological activity. The chemists have synthesized the medical polyphosphazene in 1977 with the substituent of glycine-ethylester<sup>[9]</sup>. In addition, There are applications of polyphosphazene in membrane separation, dye and catalysts<sup>[10]</sup>.

Cyclophosphazene as a kind of phosphazene compounds attracts many researchers for a long time due to their unique properties. The energetic cyclophosphazene compounds without heavy metal elements are environmentally friendly and have very high energy density. Cyclophosphazene containing amino, nitro, nitramino and azido groups would be a kind of possible high-energy compound. It is a polymer where alternate regularly with the double and single bond between the nitrogen and the phosphorus<sup>[11]</sup>. The generally accepted "island model"<sup>[12]</sup>, supposes the  $\sigma$ -bonds in the phosphazenes being formed by  $sp^3$  hybrid orbital of phosphorus. The orbital available for out-of-plane  $\pi$ -bonding is  $dyz$  orbital being combined into sets of three-center  $\pi$ -molecular orbital. These three-center orbital overlap only weakly with one another and the  $\pi$ -electrons are effectively localized in definite three-center- $\pi$ -bonds. Unusual chemical bonding in P-N backbone causes many

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unique properties of phosphazenes. There are nitrogen atoms in the heterocyclic, also the empty *d* orbital of P atom can accommodate the electrons. That made the modification to the ring possible such as adding new nitrogen heterocyclic, azido or modifying the ring by nitrification to increasing the nitrogen content. The Fig. 1.1 has showed the structure of what we talked.

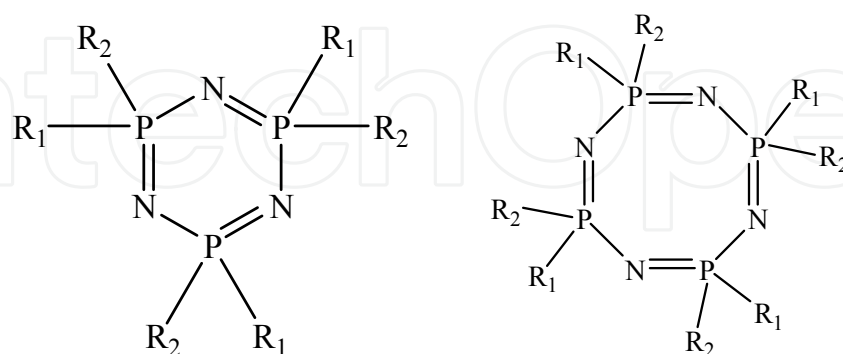


Fig. 1.1. The structure of hexa-cyclophosphazene and octa-cyclophosphazene

This structure can melt the advantages between the ignore materials and organism to form another outstanding compounds which is stable and acid and alkali resistant. Based on the N-P cross structure and the excellent flame retardant, also there will be no poison when it degrades, we can use that for the high temperature resistant. Further, we can introduce the cyclophosphazene into resin to improve this character. For example, replace the chlorine of the chlorinated- cyclophosphazene by the polymeric moiety and melt by the graphite will obtain the composite material which is ought to use in the aerospace industry [10].

Liebig [13] is the first people who had synthesis the phosphazene oligomer through  $\text{NH}_4\text{Cl}$  and  $\text{PCl}_5$  in 1834. Then people gradually studied the structure, molecular weight, chemical properties and the synthesis method in the subsequent 100 years. All jobs included the theory of synthesis and theoretical calculation.

In the development of synthesis recent 20 years, In 90s, Tuncer Hökelek of Hacettepe university have synthesized  $\text{N}_4\text{P}_4\text{Cl}_4(\text{Net}_2)_4$ [14],  $\text{N}_4\text{P}_4\text{Cl}_7(\text{OC}_6\text{H}_2-2,6-t\text{-Bu}_2-4\text{-Me})$ [15],  $\text{N}_4\text{P}_4(\text{NC}_4\text{H}_8\text{O})_6(\text{NHEt})_2$ [16] and  $\text{N}_4\text{P}_4(\text{NC}_5\text{H}_{10})_6(\text{NHEt})_2$ [17] and gave their structure parameters. Christopher W. Allen[4] and Dave[18,19] and many other scientists[20-27] have studied in this field to perfected this system. For the other aspect, it's a very rapid development for the theory development these years due to the computer technology. We got many useful data to predict the experimental result and guide the synthesis from many experts all over the world [28-37].

Our group always paid attention in the energetic materials. So how to increase the energy of this class of compounds is the point of our work. In 2008, we have reported the theoretical study for high nitrogen-contented energetic compound of 1,1,3,3,5,5,7,7-octaazido-cyclotetraphosphazene ( $\text{N}_4\text{P}_4(\text{N}_3)_8$ ) [12]. Molecular structure, vibrational frequencies and infrared intensities of it has been studied in different theoretical method. The structure has been showed in Fig. 1.2. We obtain this is a non-planar structure but there are some special characters in the P-N bonds in the nitrogen-phosphorus ring. Another paper also reported in the same year to compared with the experiment of synthesis of the 1,1,3,3,5,5-hexazido-

cyclotetraphosphazene ( $N_3P_3(N_3)_6$ ) by Michael Göbel<sup>[27]</sup> in 2006. We have anglicized the crystal in different theoretical method. The structure is in Fig. 1.3. We studied this compound about the energy gap by DFT method, the molecular activity by frontier orbital theory. Also the geometric data and the electrostatic potential has been calculated and compared by the experimental data. In 2009, we researched the 1, 1-diaminohexaazido-cyclo-tetraphosphazene (DAHA) and its isomers to perfected the theoretical study of azaido-triphosphazene<sup>[38]</sup>. In this research we point out there is no aromaticity in the ring. And we found the weakest bonds and proved different substituent affect the stability of P-N bonds in the ring. We predicted they will be a kind of right energetic materials since the high heats of formation. Fig. 1.4 has showed the five structures of the isomers. The structure of five isomers for diamino-hexaazido-cyclo-tetraphosphazene have numbered like this:

- 1,1-Diamino-3,3,5,5,7,7-hexaazidocyclotetra- phosphazene(a);  
*trans*-1,5-diamino-1,3,3,5,7,7-hexaazidocyclotetraphosphazene (b);  
*cis*-1,5-diamino- 1,3,3,5,7,7-hexaazidocyclotetraphosphazene(c);  
*trans*-1,3-diamino-1,3,5,5,7,7-hexaazidocyclotetraphosphazene(d);  
*cis*-1,3-diamino-1,3,5,5,7,7-hexa-azidocyclotetraphosphazene (e).

All the above we have talked was the azido-cyclophosphazene. For the other aspect, we have some research of the spiro-cyclotriphosphazene. Our group has synthesized 1,1-spiro(ethylenediamino)-3,3,5,5-tetrachloro-cyclotriphosphazene (ETCCTP)<sup>[39]</sup> and performed its theoretical study and the nitration product 1,1-Spiro- (N,N'-dinitro-ethylenediamino)-3,3,5,5-tetrachloro-cyclotriphosphazene (DNETCCTP). The molecular structures and crystal structures of ETCCTP have been showed in Fig.1.5. And the Fig. 1.6 showed the structure of DNETCCTP. Their structures were demonstrated by elemental analysis, NMR, MS, and FT-IR methods. We will explain these two compounds in details. Besides, the crystal of these compounds was obtained and characterized by X-ray single-crystal diffraction technique. The obtained results showed that the crystal belongs to Crystal system of Monoclinic with space group of C2/c. Based on the crystal data, the geometries and normal vibrations have been obtained by using the B3LYP method with the 6-31G\*\*, 6-311G\*\* and 6-31++G\*\* basis sets. The calculation results further demonstrate the molecular structure of the compounds.

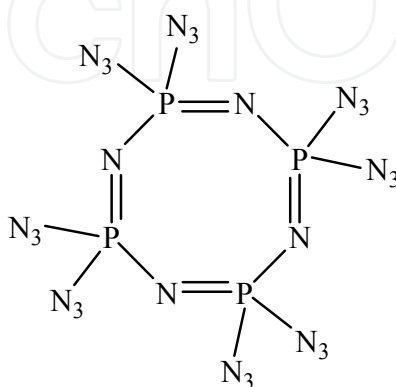


Fig. 1.2. The molecular structure of  $N_3P_3(N_3)_6$

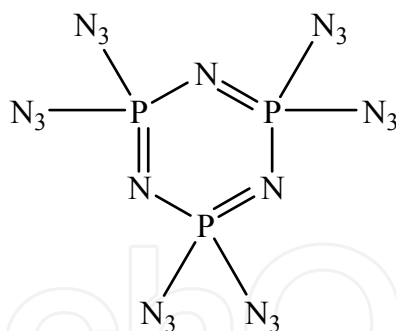
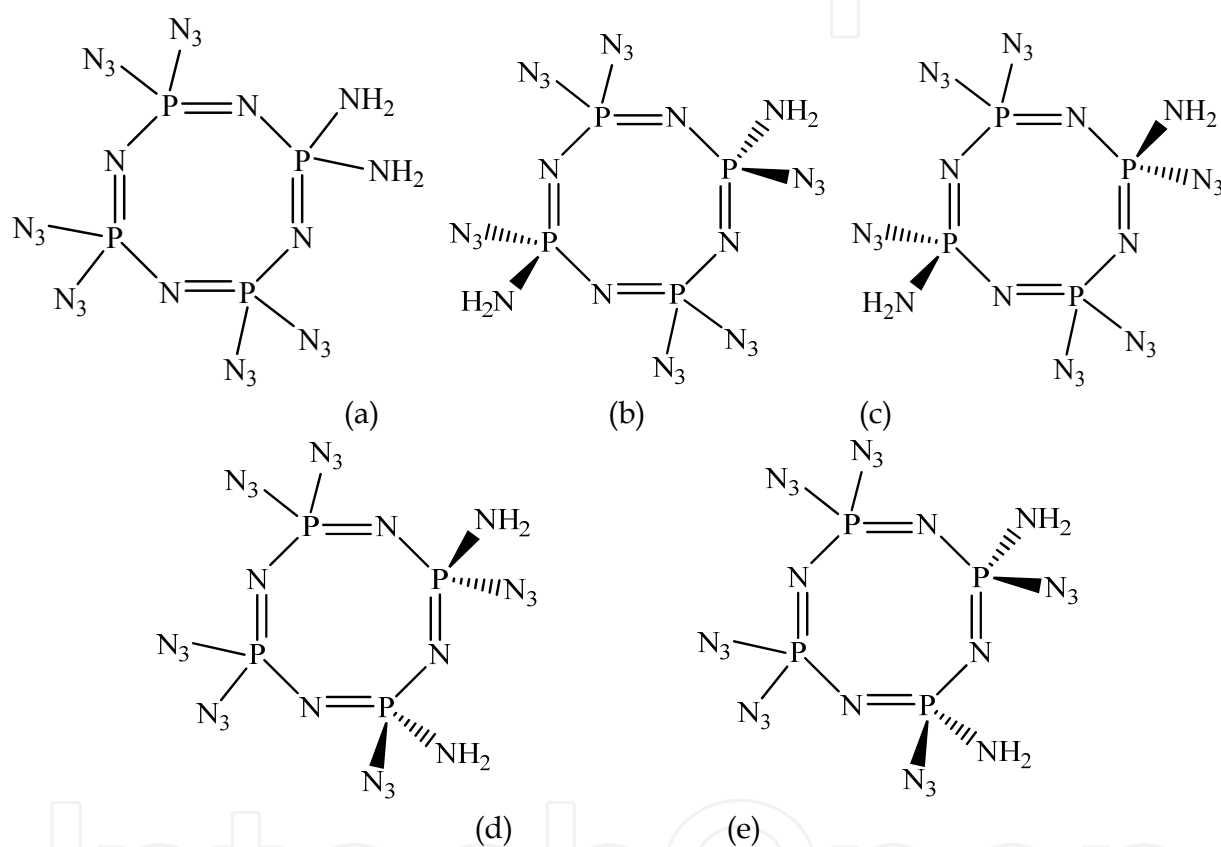
Fig. 1.3. The molecular structure of  $N_4P_4(N_3)_8$ 

Fig. 1.4. The structure of five isomers for diamino-hexaazido-cyclo-tetraphosphazene

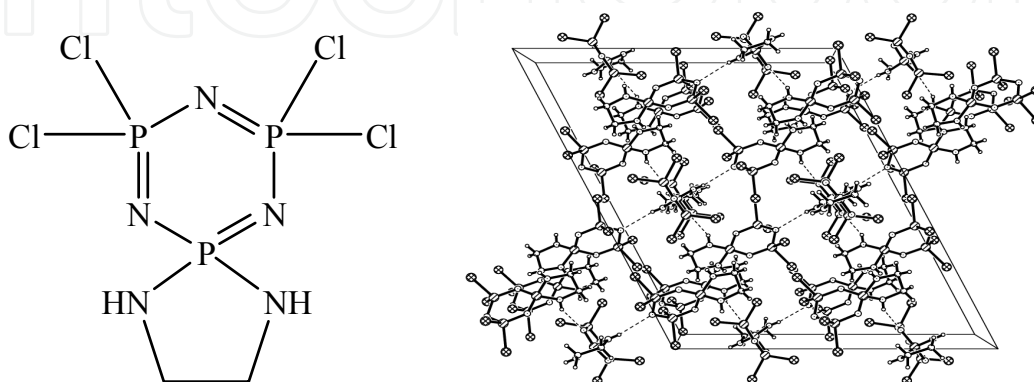


Fig. 1.5. The molecular structure and packing arrangement of ETCCTP

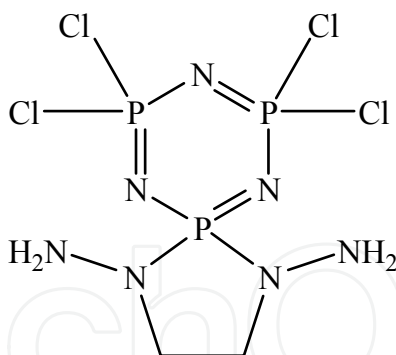


Fig. 1.6. The molecular structure and packing arrangement of DNETCCTP

The two kinds of spiro-(N,N'-dinitro-ethylenediamino)-cyclophosphazene compounds: 1,1,3,3,5,5- Tris-spiro-(N,N'-dinitro-ethylenediamino)-cyclophosphazene (3-a) and 1,1-spiro-(N,N'-dinitro-ethylene-diamino)-3,3,5,5-tetraazido-cyclophosphazene (3-b) have been investigated theoretically using HF, B3LYP and B3PW91 methods with 6-31G\* and 6-31G\*\* basis sets. Here are their structures in Fig. 1.7 and Fig. 1.8. The details you can see in section 3.1 and 3.2.

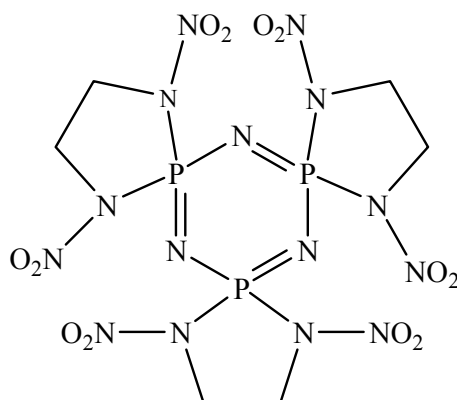


Fig. 1.7. Structure of (3-a)

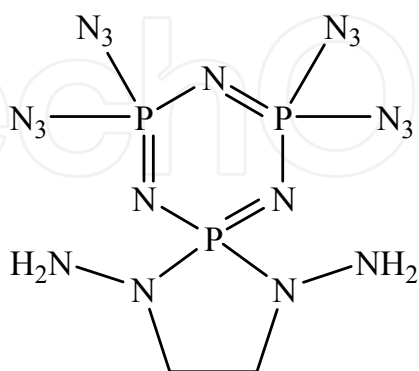


Fig. 1.8. Structure of (3-b)

In 2010, the isomers of 1,1,3,3,5,5-Trispiro (1,5-Diamino-tetrazole) Cyclo-triphosphazene (3-c) and (3-d) was pointed out to be a nice application<sup>[40]</sup>. Fig. 1.9 and Fig. 1.10 showed that. We have explained this at last in this chapter.

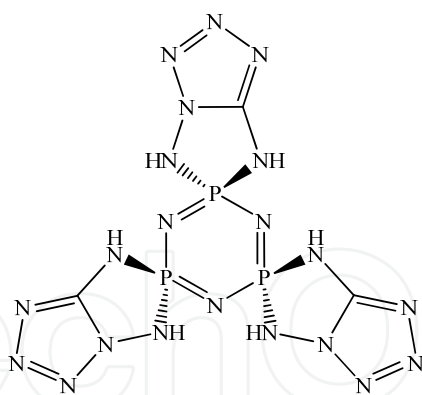


Fig. 1.9. Cis structure of (3-c)

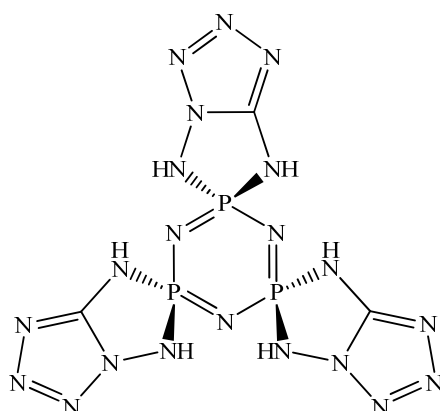


Fig. 1.10. Cis structure of (3-d)

## 2. Computational method

### 2.1 Ab initio methods

This method is an approximate quantum mechanical calculation called Hartree-Fock calculation, in which the primary approximation is the central field approximation<sup>[41]</sup>.

$$\hat{E}\psi_i = \varepsilon_i\psi_i \quad (i = 1, 2, \dots, n/2) \quad (2.1)$$

This means that the Coulombic electron-electron repulsion is taken into account by integrating the repulsion interaction. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. One of the advantages of this method is that it breaks the many-electron Schrödinger equation into many simpler one-electron equations. The other one is the approximation in HF calculations is due to the fact that the wave function must be described by some mathematical function, which is known exactly for only a few one-electron systems. In the HF equation,

$$\hat{E} = H^{core} + \sum_j (2\hat{J}_j - \hat{K}_j) \quad (2.2)$$



$\hat{H}^{core}$  means single electron Hamilton operator,  $\hat{J}_j$  is Coulombic operator,  $\hat{K}_j$  is exchange operator. So the solving process is SCF method that is a temptation and iteration. Roothaan<sup>[42]</sup> combined the atom orbital  $\chi_\mu$  to the molecular orbital  $\phi_i$  linearly (LCAO-MO).

$\phi_i = \sum_{\mu=1}^N c_{\mu i} \chi_\mu$ . After variational calculation of this deduction, we can get a secular equation showed below:

$$\sum_{\mu=1}^N (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \quad (\mu = 1, 2, \dots, N) \quad (2.3)$$

Transfer the equation to the matrix, that is  $FC = SC_\varepsilon$ . In this equation, C is MO coefficient matrix,  $\varepsilon_i$  is the energy of  $\phi_i$ , and F is Fock matrix which is means the average potential field of the electron in each orbital. The solving result is a series of MO coefficient and energy level.

A variation on the HF procedure is the way that orbital is constructed to reflect paired or unpaired electrons. If the molecule has a singlet spin, then the same orbital spatial function can be used for both the  $\alpha$  and  $\beta$  spin electrons in each pair. This is called restricted Hartree-Fock method (RHF). This scheme results in forcing electrons to remain paired. This means that the calculation will fail to reflect cases where the electrons should uncouple. We have to say that one Slater matrix wave function as the trial function of a molecular will lead to the HF equation by variation of total energy. In this method, there will be a big error although we use a high level, which is because we haven't consider the electron correlation. So there are many methods have taken account into the electron correlation such as CI, Møller-Plesset<sup>[43]</sup> ( $MP_n$ ). And the methods can give more accuracy results.

The disadvantage of *ab initio* methods is that they are expensive. These methods often take enormous amounts of computer CPU time, memory, and disk space. And presently, the density functional theory (DFT) very popular. We will talk it below.

## 2.2 Density functional theory

This theory has been developed more recently than other *ab initio* methods. Because of this, there are classes of problems not yet explored with this theory, making it all the more crucial to test the accuracy of the method before applying it to unknown.

The premise behind DFT is that the energy of a molecular can be determined from the electron density instead of a wave function. This theory originated with a theorem by Hohenberg and Kohn<sup>[44]</sup> that stated this was possible. A particle application of this theory was developed by Kohn and Sham<sup>[45,46]</sup> who formulated a method similar in structure to the HF methods.

A density functional is then used to obtain the energy for the electron density. A functional is a function of a function, in this case, the electron density<sup>[44,45]</sup>.



$$\begin{aligned}
 E_T[\rho] &= T[\rho] + U[\rho] + E_{xc}[\rho] \\
 &= -\frac{1}{2} \sum_i \int \phi_i(\vec{r}_1) \nabla^2 \phi_i(\vec{r}_1) d\vec{r}_1 + \sum_A \int \frac{Z_A}{|\vec{R}_A - \vec{r}_1|} \rho(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (2.4)
 \end{aligned}$$

$\rho$  means the electron density,  $T[\rho]$  means the kinetic energy of the system with no interaction,  $U[\rho]$  is the classic Coulomb interaction,  $E_{xc}[\rho]$  means the other energy in the total energy such as the exchange correlation energy. The next equation is the detail of the three items. The exchange correlation energy can express as<sup>[47-53]</sup>

$$E_{xc}[\rho] = \sum_{\gamma} \sum_{\gamma'} -2\pi \frac{\rho_1^{\gamma}(\vec{r}_1) \rho_x^{\gamma'}(\vec{r}_1, s)}{s} d\vec{r}_1 s^2 ds \quad (2.5)$$

$\gamma$  and  $\gamma'$  means two ways of spin. The single electron orbit  $\{\phi_i(\vec{r}_1) \ i=1, 2, \dots, n\}$  is the solution of the single electron Kohn- Sham equation.

$$\left[ \frac{1}{2} \nabla^2 + \sum_A \int \frac{Z_A}{|\vec{R}_A - \vec{r}_1|} + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + V_{xc} \right] \phi_i(\vec{r}_1) = h_{KS} \phi_i(\vec{r}_1) = \varepsilon_i \phi_i(\vec{r}_1) \quad (2.6)$$

$E_{xc}$  on the density of the derivative is  $V_{xc}$  that is the exchange correlation potential. This is the same with the molecular orbital theory, the multi-electron wave function equate the linear product of single molecular orbit, which can express like this,

$$\Psi(\vec{r}) = \left| \phi_1(1) \overline{\phi_1(1)} \phi_2(1) \overline{\phi_2(1)} \cdots \phi_{n-1}(1) \overline{\phi_{n-1}(1)} \phi_n(1) \overline{\phi_n(1)} \right| \quad (2.7)$$

The information of electron exchange and correlation are contained in the point function  $\rho_x^{\gamma'}(\vec{r}_1, s)$ , also it includes the interaction between the electron correlation and kinetic energy.  $\rho_x^{\gamma'}(\vec{r}_1, s)$  means the electron located at  $\vec{r}_1$  will repulsed other electrons to close to

itself in the range  $s$ . The repulsive energy is increased with the  $\rho_x^{\gamma'}(\vec{r}_1, s)$  increasing.

$\rho_x^{\gamma'}(\vec{r}_1, s)$  can be solved by the schrödinger equation of multi-electron system<sup>[54]</sup>. The approximate processing is start with the single electron Kohn- Sham equation, we can instead of the  $\rho_x^{\gamma'}(\vec{r}_1, s)$  by model function. It is proved there is some properties of the correlate function<sup>[50-52]</sup>:

$$4\pi \int \rho_x^{\gamma'} \left( \vec{r}, s \right) s^2 ds = 0 \quad (2.8)$$

The related Fermi function  $\rho_x^{\gamma'} \left( \vec{r}_1, s \right) (r = r')$  is satisfying the normalization condition.

$$4\pi \int \rho_x^{\gamma'} \left( \vec{r}_1, s \right) s^2 ds = 0 \quad (2.9)$$

$$\rho_x^{\gamma'} \left( \vec{r}_1, s \right) = \rho_x^{\gamma'} \left( \vec{r} \right) \quad (2.10)$$

Here 2.8 to 2.10 is the limiting condition of tectonic model function [54].

### 2.3 Mulliken population and NBO analysis

One of the original and still most widely used population analysis schemes is the Mulliken population analysis. The fundamental assumption used by the Mulliken scheme for partitioning the wave function is that the overlap between two orbitals is shared equally. This does not completely reflect the electro-negativity of the individual elements. However, it does give one a means for partitioning a wave function and has been found to be very effective for a small basis sets. A molecular orbital is a linear combination of basis functions. The integral of a molecular orbital squared is equal to 1 as normalization. The square of a molecular orbital gives many terms, which yield the overlap when integrated. Thus, the orbital integral is actually a sum of integrals over one or two center basis functions. In mulliken analysis, the integral from a given orbital are not added. Instead, the contribution of a basis function in all orbitals is summed to give the net population of that basis function. Likewise, the overlaps for a given pair of basis functions are summed for all orbitals in order to determine the overlap population for that pair of basis functions. The overlap populations can be zero by symmetry or negative, indicating anti-bonding interactions. Large positive overlaps between basis functions on different atoms are one indication of a chemical bond.

Natural bond orbital (NBO) analysis [55-58] has been carried out to complete the picture of the ring bonding system in the nitrogen-phosphorus compounds. In the NBO analysis according to references' method [58,59], in order to complete the span of the valence space, each valence bonding NBO ( $\sigma_{AB}$ ) ought to be paired with a corresponding valence anti-bonding NBO ( $\sigma_{AB}^*$ ). In the equation 2-11, the coefficient  $c_A$  means the contribution of atom A to the bond A-B, and  $h_A$  means A's atom orbital.

$$\sigma_{AB}^* = c_A h_A - c_B h_B \quad (2.11)$$

The NBO analysis is carried out by examining all possible interactions between donor Lewis-type NBOs and acceptor non-Lewis NBOs, and estimating their energies. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbital, they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E associated with delocalization  $i \rightarrow j$  is estimated as

$$E = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (2.12)$$

Where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$ ,  $\varepsilon_i$  are diagonal elements and  $F(i,j)$  is the off-diagonal NBO Fock matrix element

## 2.4 Thermodynamic function calculation

We can calculate the thermodynamic properties such as enthalpy, entropy, Gibbs free energy and chemical equilibrium constant or the composition by using Gaussian 03. Conveniently we can obtain the activation energy, pre-exponential factor and rate constant.

The standard heat of formation of an energetic compound is a very important parameter, which may be used to estimate the explosion pressure and explosion velocity. The calculation of theoretical heats of formation is split into two steps<sup>[60]</sup>. The first is to calculate the heats of formation of the molecule at 0K. It can be expressed by

$$\Delta_f H^\ominus(M, 0K) = \sum_{atoms} x \Delta_f H^\ominus(X, 0K) - \sum D_0(M) \quad (2.13)$$

where M stands for the molecule, and X to represent each element which makes up M, and x will be the number of atoms of X in M.  $\sum D_0(M)$  is atomization energy of the molecule, which is readily calculated from the total energies of the molecule ( $\varepsilon_0(M)$ ), the zero point energy of the molecule ( $\varepsilon_{ZEP}(M)$ ) and the constituent atoms:

$$\Delta_f H^\ominus(M, 0K) = \sum_{atoms} x \Delta_f H^\ominus(X, 0K) - \sum x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZEP}(M) \quad (2.14)$$

The second step is to calculate the heats of formation of the molecule at 298 K.

$$\begin{aligned} \Delta_f H^\ominus(M, 298K) &= \Delta_f H^\ominus(M, 0K) + (H_M^0(298K) - H_M^0(0K)) \\ &\quad - \sum x (H_X^0(298K) - H_X^0(0K)) \end{aligned} \quad (2.15)$$

Where  $H_M^0(298K) - H_M^0(0K)$  and  $H_X^0(298K) - H_X^0(0K)$  are the enthalpy corrections of the molecule and atomic elements, respectively. Here, the enthalpy corrections of atomic elements can be obtained from both the calculated and the experimental data<sup>[61,62]</sup>, and the enthalpy correction for the molecule is  $H_{corr} - \varepsilon_{ZEP}(M)$ , where  $H_{corr}$  is the thermal correction to enthalpy.

The calculation of the Gibbs free energy of a reaction is similar, except that we have to add in the entropy term:

$$\Delta_f G^\ominus(M, 0K) = \Delta_f H^\ominus(298K) - T(S^0(M, 298K)) - \sum S^0(X, 298K) \quad (2.16)$$

Where  $S^0(M, 298K)$  can be given by using the reaction of  $S = (H - G) / T$  and  $S^0(M, 298K)$  can be from the JANAF tables<sup>[63]</sup>.

### 3. Theoretical study on the spiro derivatives of cyclophosphazene

A large number of spiro compounds formed by the reaction of chloro-cyclophosphazene or fluoro-cyclophosphazene with difunctional reagents have been reported<sup>[64]</sup>. Muralidharan<sup>[65,66]</sup> has studied synthetical ansa-fluorophosphazene and ansa- or spiro- style substituted fluoro-phosphazene. In 1994, compound (3-a) has been synthesized by Dave<sup>[19]</sup> and its structure was confirmed by X-ray crystallography. The crystal has shown to have moderate impact sensitivity, high melting point and excellent density, and can be applied for the explosive composition. Dave has also studied the synthesis route of compound (3-b). (Fig. 1.7 and 1.8) In 2004, Magdy and others studied the synthesis route of (3-b) and the application in new primary explosive. Compound (b) was analyzed by DSC. In this section, we also design another new spiro-cyclo-phosphazene (c) (Fig. 1.9 and 1.10) maybe a good application prospect. As a part of the series of research works on high-energy-density compounds derived from cyclo-phosphazene, we performed the theoretical calculation about some spiro derivatives of cyclo-phosphazene compared by the experiment data to predict the application in energetic material in the future.

#### 3.1 1,1,3,3,5,5-tris-spiro (N,N'-dinitro-ethylenediamino) cyclotriphosphazene (3-a)

##### 3.1.1 Geometric properties

The structures and the atom serial numbers of (3-a) studied in this work are showed in Fig. 3.1. All the optimized structural characteristics calculated at HF, B3LYP and B3PW91 levels of theory for the compounds with 6-31G\* and 6-31G\*\* basis set are also calculated. As can be seen from the result, B3LYP and B3PW91 methods, used in this study, lead to similar values for bond lengths, bond angles and dihedral angles. However, the results are different from those obtained by HF method.

The phosphorus-nitrogen bond length of the ring by HF method is 1.576 Å on average, which is consistent with the literature (1.58 Å), and it is the significantly shortest. But the averaged length of P=N by the B3LYP and B3PW91 methods is 1.60 Å, which is relatively approach to cyclo-phosphazene of azido style studied before. The two P=N bond being separated is equal in the six P=N bond of the ring, and the biggest value of all the P=N bond is 0.013 Å, so we think that the P=N bond is equal in the hexa-phosphazene ring, and we know that the phosphazene ring is a total flat surface according to the bond angles having known. In the six P=N bond out the ring, because in the -NO<sub>2</sub> in connect with spiro ring, the position mindset at space is different and the stretch function to the P=N bond is different, so three pentaspiro rings are distortional and not total side, and P=N bond length in connect with the same phosphorus atom is unequal. In the six -NO<sub>2</sub> which is connect with penta ring, N-N bond length is nearly equal, with the maximum size being 0.012 Å. N=O bond length in the -NO<sub>2</sub> in connect with the same spiro ring is unequal, and N=O bond length in the same ring is unequal, which are 1.221 Å, 1.226 Å, 1.219 Å, 1.224 Å at B3LYP/6-311G\*\* level, respectively. Half of twelve N=O bonds are double bonds in the three spiro ring, and the other are delocalized bonds. Three penta-spiro rings are perpendicular to the cyclo-tri-phosphazene ring. Seen from the dihedral angle, atoms in the heterocyclic made up of N and P are in the same plane, while atoms out the heterocyclic and the heterocyclic are not coplanar.

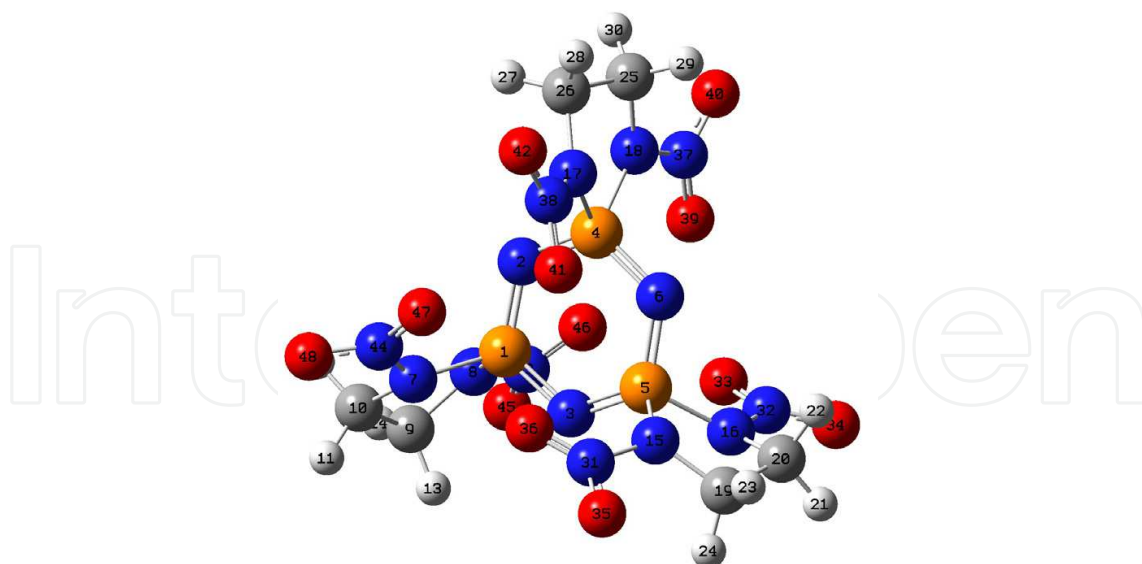


Fig. 3.1. The structure of molecular (3-a)

### 3.1.2 Vibrational analysis

The vibrational harmonic frequencies of (3-a) have been calculated using the same level of theory and basis set used in the geometry optimization, we only show the vibrational frequencies and their infrared intensities of the stationary point for (3-a) at B3LYP/6-31G\* level in Table 3.1. From the calculation, we can see there is no imaginary frequency. The result indicates that all the optimized structures correspond to the minimum point on the potential energy surface. From the result, we can see that the strongest absorption peak located at  $1324.52\text{ cm}^{-1}$ ,  $1683.43\text{ cm}^{-1}$  and  $1202.21\text{ cm}^{-1}$ . What they means  $-\text{CH}_2$  in-plane asymmetry wag,  $-\text{NO}_2$  in-plane stretching vibrational absorbing and P-N-P ring twist.

### 3.1.3 Charge distribution and bond order analysis

Table 3.2 summarizes overlap electron population of (3-a) at B3LYP/6-31G\* level. From the bond electron population, we can discover that the electron population of P=N bond in the phosphazene ring is the largest. So P=N bond in the ring exists stronger interaction and the whole phosphazene ring is more stable. The interaction of the N=O bond of  $-\text{NO}_2$  is more stronger, but the population of the N=N bond in which  $-\text{NO}_2$  is connect with three spiro rings are the smallest, so  $-\text{NO}_2$  is more lively and splits earliest from the rings. The interaction of the C-N bond in the spiro ring and the P=N bond in connect with the phosphazene ring is weaker, so they also take place to split easily.

Table 3.3 summarized the second-order perturbation estimates of “donor-acceptor” (bond, anti-bond) interactions for the couple [lone pair/N3 (or NO) anti-bond] on the basis of NBO with the limit of  $2.09\text{ kJ/mol}$  threshold. In the molecular (3-a), the interaction of the N=O bond in three spiro rings is the strongest. The interaction between the  $\sigma$  N=O anti-bond and the  $\pi$  N=O anti-bond is the strongest stabilization which can up to  $30077.86\text{ kJ/mol}$ . The interaction between the different  $\sigma$  N=O anti-bond and  $\pi$  N=O anti-bond or the  $\pi$  anti-bond and the  $\pi$  anti-bond is stronger. The N=O bond between three spiro rings has very strong area function.

$\nu$	Frequencies( $\text{cm}^{-1}$ )	Intensities ( $\text{km/mol}$ )	Assignment
1	633.53	22.68	P-N-P (ring) in-plane stretching
	634.03	20.92	
2	1043.63	283.93	N-NO <sub>2</sub> symmetry stretching
	1060.87	614.90	-CH <sub>2</sub> symmetrical wag
3	1187.41	194.44	P-N, C-N in-plane twist
	1190.80	123.59	
	1192.48	104.26	
	1194.82	268.45	
4	566.21	236.99	P-N-P ring twist
	1133.55	4.60	
	1200.98	479.36	
5	1202.21	760.71	-CH <sub>2</sub> in-plane symmetry wag
	1351.65	80.95	
6	1386.35	65.96	-CH <sub>2</sub> in-plane asymmetry wag
	1324.52	1305.60	
	1388.22	74.74	
	1389.70	432.92	
7	1677.18	131.88	-NO <sub>2</sub> in-plane stretching vibrational absorbing
	1678.42	195.52	
	1683.43	942.15	
	1689.05	836.33	
8	1703.75	22.04	-CH <sub>2</sub> symmetry stretching vibration
	3067.84	17.21	
	3074.16	13.73	
9	3088.27	11.26	-CH <sub>2</sub> asymmetry stretching vibration
	3144.39	4.50	
	3148.25	3.50	
	3160.99	2.46	
	3167.99	1.75	

Table 3.1. Vibrational harmonic frequencies in  $\text{cm}^{-1}$  and their IR intensities in  $\text{km/mol}$  of (3-a) calculated for the optimized structures at B3LYP/6-31G\* level

chemical bond	electron population	chemical bond	electron population
N32-O33	0.316	P4-N2	0.467
N32-O34	0.330	P4-N6	0.455
N31-O35	0.331	C19-C20	0.285
N31-O36	0.323	N18-C25	0.216
N17-N38	0.175	N17-C26	0.215
N18-N37	0.182	N24-H25	0.357
P5-N16	0.201	C19-H23	0.381
P5-N15	0.183		

Table 3.2. The overlap electron population of (3-a)



Donor NBO (i)	Acceptor NBO (j)	E(2)/(kJ/mol)
BD*(1)N44-O48	BD*(2)N44-O47	973.856
BD*(1)N44-O48	BD*(1)N44-O47	1174.162
BD*(2)N44-O47	BD*(2)N44-O48	1535.941
BD*(1)N44-O47	BD*(2)N44-O48	30077.859
BD*(1)N43-O46	BD*(2)N43-O45	9292.307
BD*(1)N43-O45	BD*(2)N43-O46	2751.652
BD*(1)N38-O41	BD*(2)N38-O42	12070.168
BD*(2)N37-O40	BD*(1)N37-O39	16672.432
BD*(1)N32-O34	BD*(2)N32-O33	2134.183
BD*(1)N32-O33	BD*(2)N32-O34	8571.383

Table 3.3. NBO analysis results of (3-a)

### 3.1.4 The total energy and heats of formation from computed atomization energies

The total energies, the heats of formation and the density at 298.15K are computed. The target compounds are definite A, B, C and (3-a) in terms of the number of spiro-dinitro-ethylenediamino contained, respectively. The molecule structure is showed in Fig. 3.2.

According to the data from Table 3.4, it can be found that the number of nitro has the certain influence on heats of formation of the target compounds. Among A, B, C, and 4-a, the heat of formation of A containing three spiro-ethylenediamine is the least, and the full nitration product, (3-a) has the largest value. So, they show that heats of formation of the target compounds increase with the increment of the nitro number. This is because the nitro is a high-energy group, its introduction resulted in the increase in the heat of formation of the target compounds, the level of content energies can also increase, but the target compounds stability will be reduced, become sensitive to hot and impact. We also calculated the density of a series of compounds, calculated the density of (3-a) which is 1.893 g/cm<sup>3</sup>. These values indicate that the compound would expect to contain more energy, thus may potentially be used as energetic materials.

	E <sub>0</sub> (kJ/mol)	HOF (kJ/mol)	ρ (g/cm <sup>3</sup> )
A	-4606942.85	55.21	1.52
B	-5679675.77	62.09	1.47
C	-6752288.55	94.16	2.23
3-a	-7824988.02	112.05	1.893 (1.887)

Table 3.4. The calculated total energies, heats of formation, density of target compounds at 298.15K



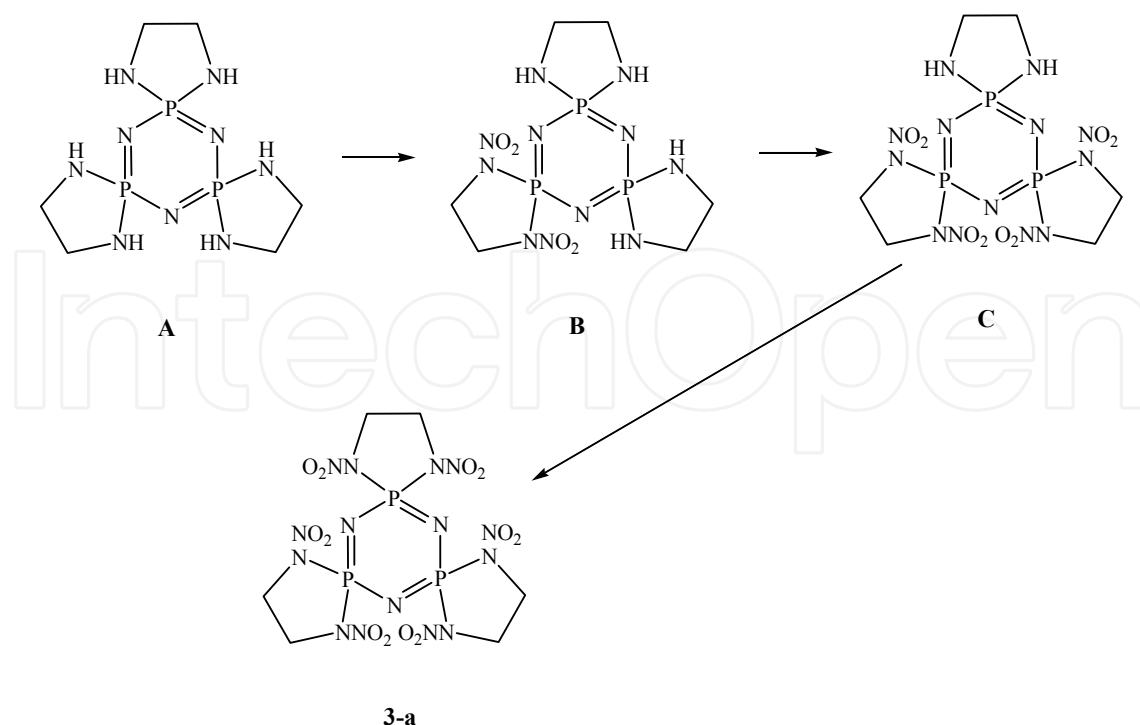


Fig. 3.2. Molecular (3-a) and its related products

### 3.2 1,1-spiro- (N,N'-dinitro-ethylenediamino)-3,3,5,5- tetraazido- cyclophosphazene (3-b)

#### 3.2.1 Geometric properties

The structure of (3-b) have been showed in Fig 3.3. From the result, three P=N bond lengths are equal in the hexa-numbered ring of (3-b), but the P=N bond length (1.594 Å) next to spiro ring is the shortest. Four azido groups have certain regulation because of the equal P=N bond by ones and twos. So they exist the equal P=N<sub>α</sub>, N<sub>α</sub>=N<sub>β</sub>, N<sub>β</sub>=N<sub>γ</sub> bonds by ones and twos. Because the stretch function is different, so that the spiro ring and azido group are the whole cyclophosphazene, the different P=N bonds make existence outside the ring and the P=N bond is obviously longer than the P=N<sub>α</sub> bond in the spiro ring. The equal N=N bonds make existence because the function that the two -NO<sub>2</sub> is to the spiro ring in the pentaspiro ring is same. But two N=O bonds are unequal in a -NO<sub>2</sub>, and the N=O bonds are equal in the different -NO<sub>2</sub>. Seen from the dihedral angle, atoms in the heterocyclic made up of N and P are in the same plane, while atoms out the heterocyclic and the heterocyclic are not coplanar.

#### 3.2.2 Vibrational analysis

The vibrational frequencies and their infrared intensities of stationary point have been showed in table 3.5. Compared with (3-a) from the result, we see they are very consistent with the experimental results. Also here is no imaginary frequency, which is proved the structure correspond to the minimum point on the potential energy surface. From the result, we can see that the strongest absorption peak is due to P-N-P ring twist and P-N, C-N in-plane twist.

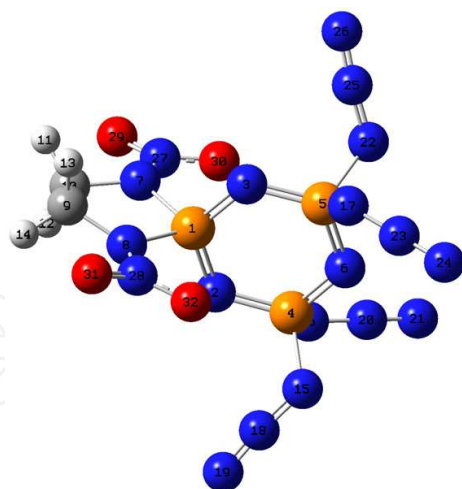


Fig. 3.3. The structure of (3-b)

$\nu$	Frequencies( $\text{cm}^{-1}$ )	Intensities (km/mol)	Assignment		
1	605.49	206.54	P-N-P (ring) in-plane stretching		
	617.16	23.61			
2	1005.33	2.30	N-NO <sub>2</sub> symmetry stretching -CH <sub>2</sub> symmetrical wag		
	1068.23	120.55			
	1118.38	3.00			
3	1201.91	1048.03	P-N, C-N in-plane twist		
	1211.08	46.99			
	1213.83	24.89			
	567.04	68.08			
4	1150.12	0.50	P-N-P ring twist		
	1224.62	1611.53			
	1360.21	95.62			
	1396.03	147.63			
	5	1322.04		280.35	-CH <sub>2</sub> in-plane symmetry wag
		1419.59		320.01	
		1534.97		3.58	
6	1326.64	226.87	N-N-N in-plane stretching		
	1327.99	795.58			
	1338.57	89.55			
	1343.62	72.39			
	2296.14	982.23			
	2298.47	630.57			
	2311.56	544.68			
	2318.88	273.00			
7	1669.76	93.44	-NO <sub>2</sub> in-plane stretching vibrational absorbing		
	1675.59	64.27			
8	3078.59	14.56	-CH <sub>2</sub> symmetry stretching vibration		
	3083.69	11.19			
9	3156.41	1.76	-CH <sub>2</sub> asymmetry stretching vibration		
	3163.90	4.29			

Table 3.5. Vibrational harmonic frequencies in  $\text{cm}^{-1}$  and their IR intensities in km/mol of (3-b)

### 3.2.3 Charge distribution and bond order analysis

As we have mentioned above, in compound (3-b), the interaction between two N=O bonds in connection with a nitril is the strongest stabilization, 15168.42 kJ/mol, this indicates that the electronics transferring tendency on of molecule orbits of the N=O bond is bigger, this is mainly because the lone pair electronics of oxygen atom have strong interaction, and two N=O bonds present to leave an area form. The interaction between the N=N bond in the spiro ring and the C-C bond in the ring is weaker stabilization, 7.52 kJ/mol. There exists the stronger interaction between lone pair electrons in the  $N_{\alpha}$  of four azido groups and the  $\pi N_{\beta}$ - $N_{\gamma}$  anti-bond, but the interaction between the P- $N_{\alpha}$  bond and the whole phosphazene ring is weaker, this indicates that azido groups split easily. Table 3.6 have showed the overlap electron population of (3-b) at B3LYP/6-31G\* level.

In this compound, the interaction at the end of the azido group is the strongest, and the population of they  $N_{\beta}$ = $N_{\alpha}$  bond is the largest and the stablest. The P=N bond in the phosphazene ring is the second. The interaction of the P=N bond in the phosphazene ring is the weakest, and split most easily while being stimulated by the external world. The spiro ring opens. The azido group also split easily, but the N=O bond in the spiro ring exists delocalization and more stable. The result of the NBO analysis has been listed in table 3.7.

chemical bond	electron population	chemical bond	electron population
N6-P5	0.483	N8-N28	0.198
N3-P5	0.458	N28-O32	0.328
N22-P5	0.275	N28-O31	0.338
N16-P4	0.278	N23-N24	0.596
N5-P22	0.275	N18-N19	0.595
P1-N8	0.177	N8-C9	0.217
P1-N7	0.177	C9-H13	0.378
N7-N27	0.198		

Table 3.6. The overlap electron population of (3-b)

Donor NBO (i)	Acceptor NBO (j)	E(2)/(kJ/mol)
BD*(2)N28-O32	BD*(2)N28-O31	703.4522
BD*(2)N28-O31	BD*(1)N28-O32	15132.1852
BD*(2)N27-O29	BD*(1)N27-O30	15168.4258
BD*(1)N27-O29	BD*(1)N27-O30	1255.5048
LP(2)N16	BD*(2)N20-N21	429.3278
LP(2)N15	BD*(2)N18-N19	432.2956
BD*(1)N28-O31	BD*(1)N28-O32	1253.9582
BD*(3)N25-N26	BD*(1)P5-N22	27.0446
BD*(3)N23-N24	BD*(1)P5-N17	27.0446
BD*(1)N7-N27	BD*(1)C9-C10	7.524
BD*(1)N7-N27	BD*(1)P1-N2	4.7652

Table 3.7. NBO analysis results of (3-b)

### 3.2.4 The total energy and Heats of formation from computed atomization energies

Compared with what we have discussed in section 4.1.4, the heat of formation of (3-b) is much larger than the (3-a), containing three spiro-dinitro-ethylenediamino, mainly due to the existence of azido groups. It explains that azido groups content energy is higher and more unstable than nitryl. As talking the density about them, We calculated the density of (3-b) is 1.920 g/cm<sup>3</sup>, which is bigger than (3-a), 1.893 g/cm<sup>3</sup>. That is very consistent with the crystal density of the literature. These values indicate that these two compounds would expect to contain more energy, thus may potentially be used as energetic materials. The details have been showed below (Table 3.8).

Parameters	Value
E0 (kJ/mol)	-6382918.40
HOF (kJ/mol)	328.40
$\rho$ (g/cm <sup>3</sup> ) (experimental)	1.920 (1.830)

Table 3.8. The calculated total energies, heats of formation, density of (3-b)

## 3.3 1,1,3,3,5,5-Tris-spiro (1,5-Diamino-tetrazole) Cyclotriphosphazene and its isomers.

### 3.3.1 Geometric properties

Two isomers will be produced when 1,5-diamino-tetrazole (DAT) reacted with hexa-chlorin-cyclotri-phosphazene. The reason for this is the different location of C atom of the tetrazole. You can see the molecular structure of them in Fig 3.4. (3-c) and (3-d) are the two isomers of the title compound. We optimized by AM1 in the first time, and at last, we got the optimization by using B3LYP and B3PW91 methods with 6-31G\* and 6-311G\*\* basis set. From the calculated data, we proved the two can exist stably.

We see the cyclotriphosphazene ring is nearly coplanar from the dihedral values. Different methods and basis sets would get similar result, the maximum error is 0.01 Å. The basic data of the structure is nearly equal. We will take the cis structure for analysis.

The result told us the length of bond P-N is always equal to each other, the average is 1.607 Å, which is similar to the length of the same bond in N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>. The hydrogen of the amino of the DAT will lost with two chlorine of N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> when react is in the process. So there is no same length to the bond N-P in the quinaryring such as 1.709 Å to P<sub>5</sub>-N<sub>13</sub>, but 1.747 Å to P<sub>5</sub>-N<sub>12</sub>. The bond N-P have the same length when the nitrogen connecting with the phosphorus of the cyclotri-phosphazene ring. The length of P3-N20 is equal to P1-N27, the same to P1-N26 and P3-N19. The length of N-H, N-N and C-N are equal at the corresponding positions. The calculated result of the bond length of the tetrazole is consistent to the experimental data. The length of N18-N14, N14-N15, N15-N16 are 1.362 Å, 1.293 Å, 1.382 Å respectively, the corresponding data of the experiment were 1.363 Å, 1.279 Å, 1.367 Å. That's to say our calculation and prediction is correct and credible. Compared the bond of N18-N19 (1.400 Å) and N18-N14 (1.362 Å), the former is greater than the latter that is due to the conjugate function between the quinaryring and the tetrazole. And this effect makes the bond length average and the electron delocalization. Also this is a stable state. The angle of the N20-C17-N18 or N19-N18-N14 are between 93°~117° instead of the 120° caused by sp<sup>2</sup> hybrid of N and C. That is to say there is the tension between the two ring.

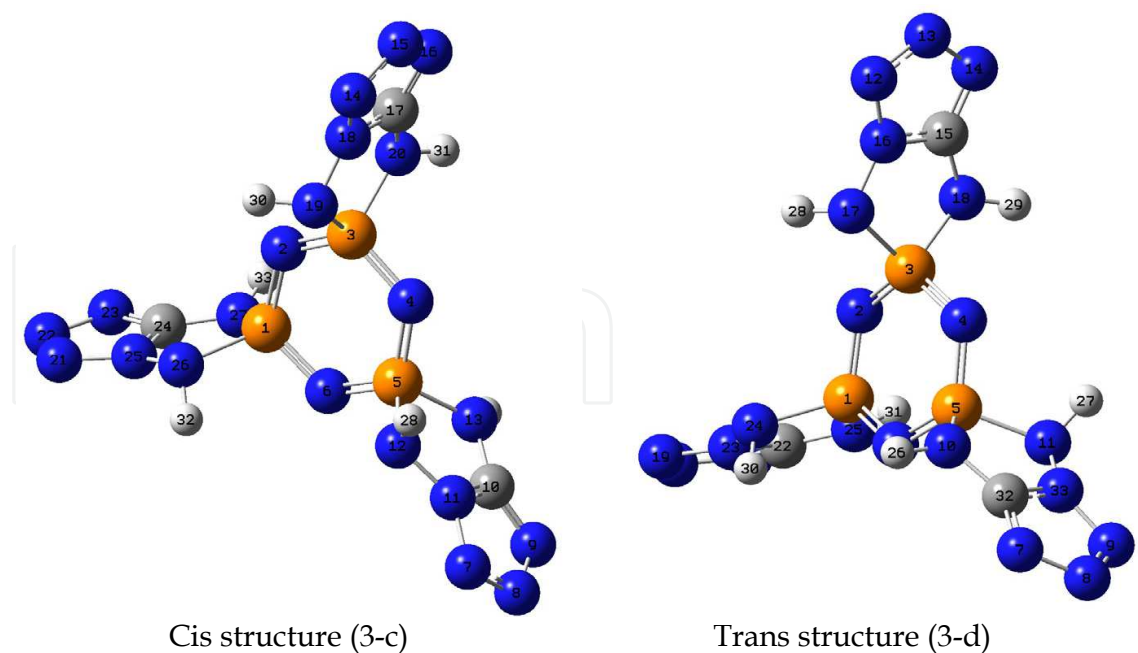


Fig 3.4 The structure of two isomers of the title compound

### 3.3.2 Vibrational analysis

No imaginary frequency in the vibrational calculation, So they're the minimum point of the potential energy surface. That's to say they are all the stable structure. We have obtained 93 IR frequencies and their intensity, 12 in which has greater intensity. We did the simulation shown in Fig.3.5 and 3.6.

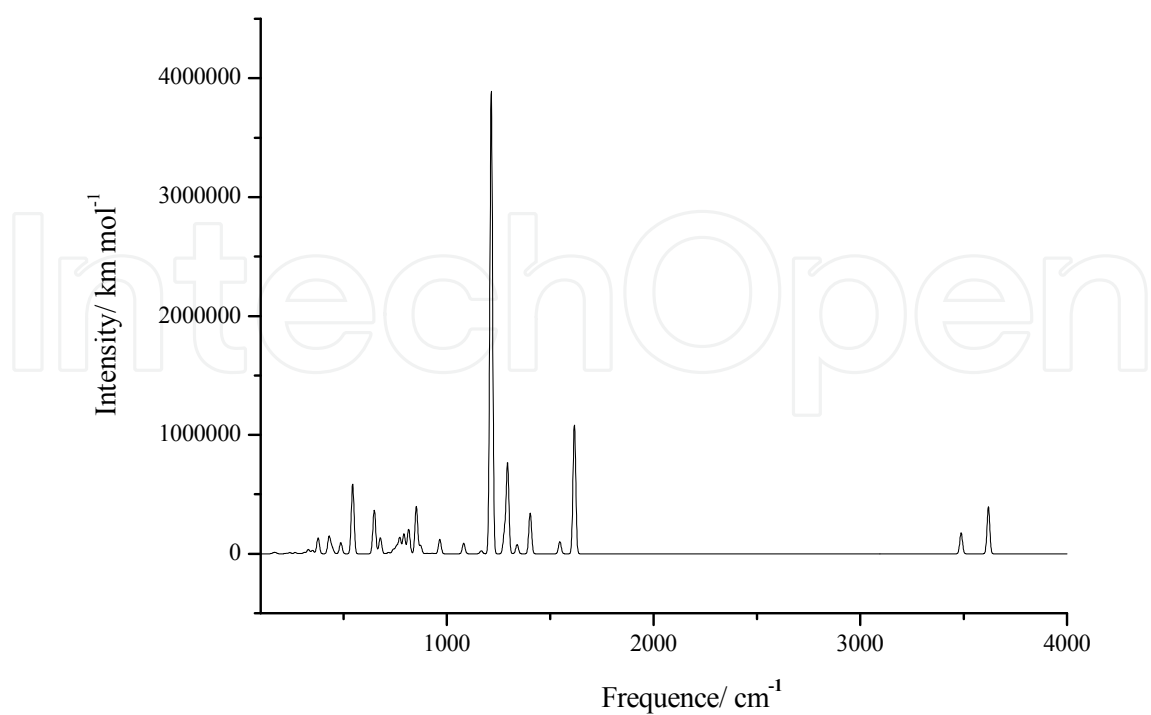


Fig. 3.5. The IR spectrum of (3-c)

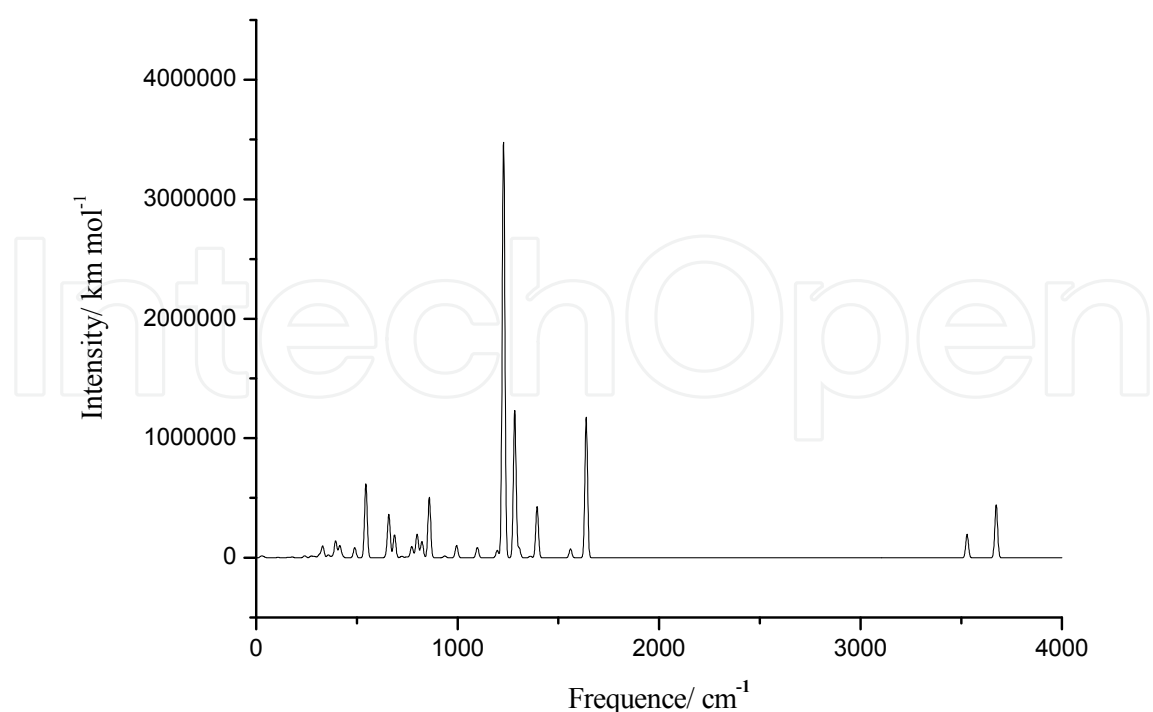


Fig. 3.6. The IR spectrum of (3-d)

We analyzed the cis structure to explain the vibrational frequency and infrared intensities. The N-H stretching vibration is in the high frequency region near by  $3400\text{cm}^{-1}$  or  $3600\text{cm}^{-1}$ . So there are 2 lines in the high frequency region. The C-N stretching vibrational intensity between the DAT and the quinaryring is around  $1600\text{cm}^{-1}$ . Its in-plane stretching vibrational region is from  $1546\text{cm}^{-1}$ . In-plane stretching vibration of bond N-H and the stretching of N-N at the ring is at the region between  $1270\sim 1400\text{cm}^{-1}$ . The intensity of the strongest vibration absorption for the bond P-N stretching is up to  $1351\text{ km/mol}$ . The twist of the cyclophosphazene ring, bending of the N-H and in-plane rocking located at  $900\sim 1200\text{cm}^{-1}$ . In Fig 3.6, we can see a very similar IR spectrum picture with the Fig 3.5.

### 3.3.3 Charge distribution and bond order analysis

The overlap population has been showed in Table 3.9. The two isomers have the similar performance. The bond N-N between the quinaryring and the DAT has the lower value. The same trend is also appeared on the bond N-N in the DAT. That's means it's easy to destruct when the ring is heat or done by the external force. Also means the bond energy is weak here. The population of bond P-N of the cyclophosphazene is up to 0.465 in average. So there is strong interaction between these bonds, which decided the ring is very stable. But to the contrary, the bond N-P out of the ring is much weaker than the same bond in the ring. For example, The population of the P1-N2 is 0.459, but only 0.259 to P1- N27. We will discuss the this phenomenon from the NBO analysis. As the delocalization, the population of bond C-N is bigger than the it of bond N-N from the result. That's consistent with the structure analysis.

The stabilization energy  $E(2)$  for each donor NBO(i) and acceptor NBO (j) are associated with  $i \rightarrow j$  delocalization, which is estimated by the calculation. We can review it in section



3.1.3 what we said before. From the data listed in table 3.10, the interaction of  $\pi^*$ -N-N and  $\pi^*$ -C-N in the DAT ring can be up to 233.67 kJ/mol. The lone electron of N atom such as N11, N18, N25 used by the tetrazole rings and quinaryring connecting with antibonding orbitals of N-N usually have a big value. This is also prove a existence of the delocalization of the DAT. The electrons between bond N-N or C-N are in domain forms. Conjugate function effects the tetrazole and quinaryring when we see the E(2) value decided by lone electron of N atom of C-N and the  $\pi^*$ -C-N is 152.15 kJ/mol. E(2) between the lone electron of N atom of the quinaryring and the  $\sigma^*$  P-N is only 2.717 kJ/mol. It's consistent with the conclusion about the stability of the molecular what we talked about before.

bond	B3LYP/6-31G*		B3LYP/6-31G**		B3PW91/6-31G*		B3PW91/6-31G**	
	Cis-	Trans-	Cis-	Trans-	Cis-	Trans-	Cis-	Trans-
N <sub>4</sub> -P <sub>3</sub>	0.460	0.458	0.457	0.455	0.462	0.46	0.459	0.457
N <sub>4</sub> -P <sub>5</sub>	0.469	0.470	0.467	0.468	0.471	0.472	0.469	0.470
N <sub>6</sub> -P <sub>1</sub>	0.469	0.468	0.467	0.467	0.471	0.469	0.469	0.468
N <sub>2</sub> -P <sub>1</sub>	0.460	0.458	0.458	0.455	0.463	0.460	0.459	0.457
N <sub>19</sub> -P <sub>3</sub>	0.246	0.244	0.236	0.234	0.254	0.250	0.243	0.240
N <sub>20</sub> -P <sub>3</sub>	0.283	0.282	0.277	0.276	0.286	0.286	0.281	0.281
N <sub>18</sub> -N <sub>19</sub>	0.168	0.171	0.165	0.168	0.166	0.168	0.162	0.164
C <sub>17</sub> -N <sub>20</sub>	0.317	0.317	0.316	0.315	0.316	0.315	0.315	0.315
C <sub>17</sub> -N <sub>18</sub>	0.306	0.306	0.302	0.302	0.302	0.301	0.297	0.297
N <sub>18</sub> -N <sub>14</sub>	0.167	0.167	0.165	0.165	0.150	0.150	0.149	0.149
N <sub>14</sub> -N <sub>15</sub>	0.246	0.247	0.245	0.246	0.239	0.239	0.238	0.238
N <sub>15</sub> -N <sub>16</sub>	0.252	0.251	0.252	0.251	0.252	0.251	0.252	0.252

Table 3.9. The selected overlap population of (3-c) and (3-d)

### 3.3.4 The total energy and heats of formation from computed atomization energies

The HOF has been calculated by B3LYP and B3PW91 method at 298 K. the result is listed in Table 3.11. Since no experimental values can be compared, we choose the DAT and hexachloro-cyclophosphazene as contrast. The HOF of hexachloro-cyclophosphazene is negative, while it of the title compound and its isomer are positive. That's to say this two structure is metastable in the chemical reaction. The two groups of data is relatively close. The HOF of trans structure is slightly larger than the cis one. That means cis structure is more stable. We also calculate the HOF of DAT lonely to get the conclusion that the two have lower energy. It is mainly due to the N atom which will increase the HOF. So the stability is relatively poor for this reason. We also studied the total energy and the frontier orbital energies of the two isomers, DAT and the hexachloro-cyclophosphazene. The data was listed in Table 3.12. The total energy of the cis structure is less than it of the trans one. But the sequence is just the opposite to the energy gap. This also explained the stability of the cis structure is better than the trans.



Orbit of Donor (i)	Orbit of Acceptor (j)	E(2) (kcal mol <sup>-1</sup> )
BD*(2)N21-N22	BD*(2)N23-C24	55.81
BD*(2)N14-N15	BD*(2)N16-C17	55.90
BD*(2)N7-N8	BD*(2)N9-C10	55.87
LP(1)N27	BD*(2)N23-C24	36.42
LP(1)N25	BD*(2)N23-C24	52.59
LP(1)N25	BD*(2)N21-N22	34.87
LP(1)N20	BD*(2)N16-C17	36.36
LP(1)N13	BD*(2)N10-C9	36.36
LP(1)N18	BD*(2)N16-C17	52.54
LP(1)N18	BD*(1)N19-P3	0.65
LP(1)N25	BD*(1)N26-P1	0.67
BD(2)N23-C24	BD*(2)N21-N22	23.53
BD(2)N16-C17	BD*(2)N14-N15	23.53
BD(1)N6-P1	BD*(1)N26-P1	2.53
BD(1)N2-P3	BD*(1)P1-N27	1.07
LP(1)N2	BD*(1)P1-N6	11.80
LP(1)N2	BD*(1)P3-N4	12.09

Table 3.10. The selected calculated NBO results of (3-c) at B3LYP/6-31G\* level.

Compounds	B3LYP/6-31G*	B3LYP/6-31G**	B3PW91/6-31G*	B3PW91/6-31G**
3-c	1725.82	1670.5	1661.68	1604.31
3-d	1728.49	1673.22	1661.89	1606.99
DAT	442.21	407.9	440.12	405.89
(N <sub>3</sub> PCl <sub>2</sub> ) <sub>3</sub>		-812.12 (experimental)		

Table 3.11. The formation heats of (3-c) and (3-d) in different methods and basic sets

Compounds	E <sub>total</sub>	E <sub>LUMO</sub>	E <sub>HOMO</sub>	Δ E <sub>L-H</sub>
DAT	-967707.99	-9.29	-645.52	636.08
(N <sub>3</sub> PCl <sub>2</sub> ) <sub>3</sub>	-10359846.98	-250.10	-809.98	559.75
3-c	-6010672.73	-101.67	-751.22	649.45
3-d	-6010669.84	-105.26	-750.44	644.99

Table 3.12. The total energy and frontier orbital energy of different compounds in B3LYP/6-31G\*

#### 4. Conclusion

In this chapter, we have summarized the spiro derivatives of cyclophosphazene. We calculated the geometric, frequency and thermodynamics constant. We analyzed the charge distribution and the national bond orbitals (NBO) and multiple overlap to judge its molecular stability. Some crystal had been synthesized when we do the theoretical study.

We explained the other category in part 3. Three materials and four structures analyzed by us. The first two compounds are non-planar. The screw ring distorted but the space orientation of the azido is the same with the structure of that of (3-a). Strong delocalization effect of N-O of the screw ring may lead to the bond breaking between the two rings. The theoretical density of the two is 1.893 g/cm<sup>3</sup> and 1.920 g/cm<sup>3</sup> respectively. The thermodynamics analysis showed the molecular (3-b) has higher energy for the proportion of azido compared to (3-a). Two isomers of 1,1,3,3,5,5-tris-spiro (1,5-Diamino-tetrazole) cyclotriphosphazene summarized at last in this chapter. The geometric analysis showed the hexacyclophosphazene is nearly planar. And the angle between the DAT and 5-membered ring is 180°. And they are nearly vertical to the cyclophosphazene ring. And the introduction of DAT increased the nitrogen content of the cyclophosphazene, so to the HOF. The electron analysis showed the cis structure is more stable than the trans one.

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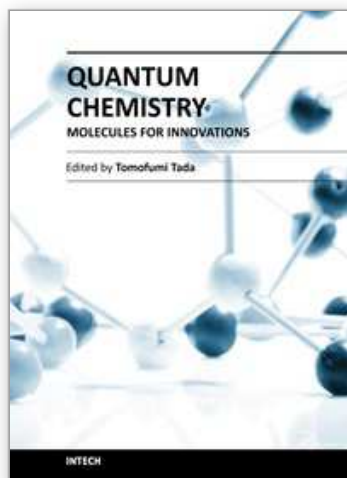
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## **Quantum Chemistry - Molecules for Innovations**

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Molecules, small structures composed of atoms, are essential substances for lives. However, we didn't have the clear answer to the following questions until the 1920s: why molecules can exist in stable as rigid networks between atoms, and why molecules can change into different types of molecules. The most important event for solving the puzzles is the discovery of the quantum mechanics. Quantum mechanics is the theory for small particles such as electrons and nuclei, and was applied to hydrogen molecule by Heitler and London at 1927. The pioneering work led to the clear explanation of the chemical bonding between the hydrogen atoms. This is the beginning of the quantum chemistry. Since then, quantum chemistry has been an important theory for the understanding of molecular properties such as stability, reactivity, and applicability for devices. This book is devoted for the theoretical foundations and innovative applications in quantum chemistry.

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