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Theoretical investigation on carbon-centered tri-*s*-tetrazine and its 10 derivatives

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Abstract

A novel species, carbon-centered tri-*s*-tetrazine ($C_4N_9H_3$), and its 10 derivatives (C_4N_9–R_3, where R = OH, F, CN, N_3, NH_2, NO_2, N=NH, N_2H_3, C≡CH, and CH=CH_2) have been studied computationally. Density functional theory (DFT) has been used to study the geometries, electronic structure, harmonic vibrational frequencies, ionization energies of the 11 compounds at the restricted (for neutrals) and the unrestricted (for cations) B3LYP/cc-pVDZ level of theory. Atoms in molecule (AIM) and natural bond orbital (NBO) analyses have been used to obtain the bonding properties. Valence bond (VB) theory is applied to explain the unusual pyramidal structure around the carbon-center and electron arrangements of orbitals. We found: (1) All the species possess novel bonding features and geometrical structures. The atoms on the periphery of each species are sp^2 hybridized. Each of these atoms offers an orbital to form an extensive conjugation system $_{12}\pi^{15}$ (a π system consisting of 12 centers and 15 electrons). The central carbon atom C13 is sp^3 hybridized, which makes the non-planar molecule shape like a straw–hat. Atom C13 also participates in the conjugated π system with its sp^3 hybridized orbital, thus forming an extensive $_{13}\pi^{16}$ conjugate π system covering the whole C_4N_9 framework. (2) The change of charge on C13 is the largest among all the atoms when the species is ionized and the atomic charges are redistributed. In other words, C13 is the attack center for electrophilic agents. Thus, the species is carbanion-like. (3) All the species have low ionization energies (IEs). The electron ionized mainly comes from C13. They may have wide applications in organic chemistry, in organometallic chemistry and in alkyl lithium chemistry once they are synthesized.
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1. Introduction

Compounds 1,2,4,5-tetrazines (i.e. *s*-tetrazines) are well known to act as electron deficient dienes in Diels–Alder reactions [1–9] with electron-rich dienophiles such as alkynes. They are useful in the synthesis of highly substituted pyridazines, heterocycles, and substituted benzenes as well as in the preparation of rigid molecular receptors [1–9]. Trend in reactivities of tetrazines has been explored in detail by Boger and co-workers [8]. Of these, the substituted *s*-tetrazines are the most reactive and most widely utilized heterocyclic azadienes. Typically, symmetrical *s*-tetrazines are employed frequently

because of their synthetic accessibility, while synthetic study has been focused only on their relative reactivities.

Correspondingly, highly symmetrical heterocyclic azadienes, *s*-triazine-based compounds, have been studied extensively. It was also found that theses compounds have various applications in production of polymers, dyes, explosives, pesticides, and commodity chemicals [10]. Among all the *s*-triazine-based compounds, Pauling and Sturdivant [11] suggested a common nucleus, three coplanar fused *s*-triazine rings. In the past decade, the tri-*s*-triazines were studied in detail, both experimentally [12–16] and theoretically [17–21]. In this work, we study a framework consisting of three fused *s*-tetrazines, i.e., tri-*s*-tetrazines ($C_4N_9H_3$) (Fig. 1). Our results show that the planar tri-*s*-tetrazines does not correspond to a local minimum on the potential energy surface, as it has one or more imaginary vibrational frequencies. The reason is most likely that the central carbon atom C13 is sp^3 hybridized and is linked to only three

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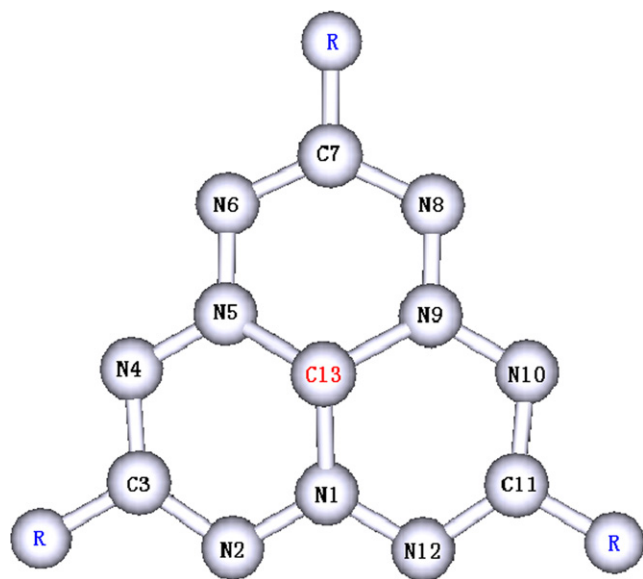*E-mail address:* bhnbwong@cityu.edu.hk (N.-B. Wong).

Fig. 1. The geometrical structure and atomic labeling of tri-*s*-triazine, where R = OH, F, CN, N_3, NH_2, NO_2, N=NH, N_2H_3, C≡CH, and CH=CH₂.

single bonds. In order to eliminate the imaginary frequencies, we have to relax the planarity constraint. As a result, each of the 11 species features a pyramidal central carbon atom C13, which rather unexpectedly bears some extra electronic charge. The existence of extra electronic charge on the central carbon atom renders the species much more reactive. The high reactivity of the tri-*s*-tetrazines may be useful in the synthesis of heterocyclic compounds. Hence, we have undertaken a study on these potentially useful compounds. To our knowledge, this is the first report on the species.

Carbanion is an anion in which the carbon has an unshared pair of electrons; it usually forms three covalent bonds and hence has eight electrons in its valence shell. The carbanion exists commonly in a trigonal pyramidal geometry. It is a reactive intermediate [22–24] and is often encountered in organic chemistry (for instance, in the E1cB elimination reaction [25]), in organometallic chemistry (for instance, in Grignard reaction [26–34]) or in alkyl lithium chemistry. Many experiments demonstrate that stable carbanions do exist [22–35]. However, they have not been isolated, possibly due to their high reactivities [28–30,35]. Substantial efforts have been made to prepare and characterize stable carbanions experimentally [31–34]. On the other hand, theoretical study on carbanions is less extensive than those on neutrals and cations, partly due to the debate on charge partitioning in a species. Carbanions can take part in many reactions such as nucleophilic addition reactions, electrophilic substitution reactions, aromatic nucleophilic substitution reactions, rearrangement reactions and elimination reactions, etc. Carbanions may also have applications in the field of molecular materials such as electrical conductors and nanomaterials. Discovering stable, separable carbanions remains a challenge to both experimental [29] and theoretical scientists. The present theoretical study on tri-*s*-tetrazines, which are stable neutral species with carbanion-like features, is another attempt towards this goal.

2. Methods

The aim of our work is to study the geometric and electronic structures and properties of tri-*s*-tetrazines using theoretical approach. The properties of tri-*s*-tetrazines will be investigated at the RB3LYP/cc-pVDZ level of theory. The central atom C13 is the focus of our discussion because the properties of the species depend largely on this atom. The substituents for tri-*s*-tetrazines chosen in this work include OH, F, CN, N_3, NH_2, NO_2, N=NH, N_2H_3, C≡CH and CH=CH₂. It is noted that the three hydrogen atoms in each of the tri-*s*-tetrazine are substituted by the same functional group.

As mentioned previously, the three rings in tri-*s*-tetrazines (either the neutrals or the cations) are not coplanar. However, the atoms on each six-member ring are essentially coplanar. Indeed, for the parent tri-*s*-tetrazine, $C_4N_9H_3$, among the 13 heavy atoms, 9 of them (i.e., except, N1, N5, N9 and C13) are practically coplanar (denoted as plane-1). The three two-ring conjoint atoms, N1, N5 and N9, form another plane, denoted as plane-2, which is slightly above plane-1. The central carbon atom C13 is about 0.6 Å above plane-1, and plane-2 is about 0.15 Å above plane1. In other words, plane-2 is between plane-1 and C13. The molecule is shaped like a straw–hat. Such a novel structure is mainly caused by the electron arrangement and the hybridization of the C13 orbitals. So, an orbital analysis based on the VB theory will be presented to explain the calculated results.

Density functional theory (DFT) has been applied to optimize the structures of the species and to calculate the harmonic vibrational frequencies. Becke's three-parameter non-local exchange functional along with the Lee–Yang–Parr non-local correlation functional (B3LYP) is employed. Dunning's cc-pVDZ basis set has been used throughout, and the SCF convergence criterion is set to 10^{-8}. There is no imaginary frequency for all of the structures optimized, suggesting that all of the structures, neutrals and cations alike, are local minima on the respective potential energy surfaces. All calculations were carried out using the GAUSSIAN03 program [36]. Natural bond orbital (NBO) [37–40] analysis has been carried out at the restricted and unrestricted B3LYP/cc-pVDZ level on the basis of the optimized geometries.

Topological property of the electronic charge density was characterized using the atoms in molecule (AIM) theory of Bader [41] with the AIM 2000 program package [42]. The AIM approach is a rigorous procedure based upon the topology of electronic density $\rho(r)$ to partition the molecule into atomic fragments Ω bound by a zero flux surface for the gradient vector field of $\rho(r)$. A crucial element of the theory is the set of properties of the critical points in $\rho(r)$, where $\triangledown\rho$ vanishes.

As our contribution, we will study the atomic charge to determine the electrophilic centers of the species. In AIM theory of Bader, molecular property is simply the sum of the corresponding atomic property [43], which is defined as volume integrals over the atomic basin Ω of property density, for example, atomic charge discussed in this work. Actually, topological analysis of electron density in AIM has been proven to be an attractive method to extract chemical insight from modern *ab initio* wave functions. This method is currently used

as an interpretative tool for many areas ranging from high-resolution crystallography to mineralogy, transition-metal chemistry and biochemistry [44]. However, most AIM applications incorporate only critical point information and visual representations of the electron density gradient vector field. Of the atomic properties, such as energy, dipolar polarization and distributed polarisability, the atomic charge should receive most attention since it continues to play a dominant role in chemical reactions and chemical interpretation of charge distribution and charge transfer, which can be used to determine the reaction site, inside a molecule. It has been shown that the partition technique of AIM theory is a reliable method to obtain the atomic charge distribution, and hence the chemical reactivity, of a molecule [43,44].

To estimate the reactivity of the 11 species studied, their ionization energies (IEs) are calculated. The IE is one of the most relevant data in thermochemical measurements. Similar to the atomic charge, it also affects the feasibility of electron transfer or oxidation-reduction processes. In quantum chemistry, accurate IEs can be obtained from high-level calculations, such as CCSDT, with a series of elaborate energy corrections [45]. However, it is impossible to calculate the IE of a molecule with the size of tri-s-tetrazines at the aforementioned computational level. In order to obtain the adiabatic IEs of the molecules, the structures of the monovalent cations are optimized at the UB3LYP/cc-pVDZ level of theory. As a rough estimation, the difference of total energies $E_{cation} - E_{neutral}$ is taken as the IE of the neutral.

The relative stabilities of molecules are usually estimated by their heats of formation (ΔH_f). A well-known method for calculating ΔH_f is the recently proposed G3 model of theory [46]. However, it is impractical to calculate the ΔH_f's of molecules with the size of tri-s-tetrazines using the G3 model. In this work, the ΔH_f values are calculated at the B3LYP/cc-pVDZ level using our previous scheme [47].

3. Results and discussion

The geometrical optimizations were successfully performed at the restricted and unrestricted B3LYP/cc-pVDZ levels. All of the vibrational frequencies of the 11 species, including their monovalent cations, are positive (not listed). Based on symmetry (C_3 symmetry for R = OH, N$_3$, N=NH, N$_2$H$_3$, and CH=CH$_2$, and C_{3v} for R = H, F, CN, NH$_2$, NO$_2$, and C≡CH), the atoms on the framework can be categorized into four sets, **AS1**: N1, N5, N9; **AS2**: N2, N4, N6, N8, N10, N12; **AS3**: C3, C7, C11; **AS4**: C13. Accordingly, the bonds can be categorized into three sets, **BS1**: N1–N2, N1–N12, N4–N5, N5–N6, N8–N9, N9–N10; **BS2**: N2–C3, C3–N4, N6–C7, C7–N8, N10–C11, C11–N12; **BS3**: N1–C13, N5–C13, N9–C13. The bond angles can also be categorized into four sets, **BA1:** N1–N2–C3, C3–N4–N5, N5–N6–C7, C7–N8–N9, N9–N10–C11, C11–N12–N1; **BA2:** N2–C3–N4, N6–C7–N8, N10–C11–N12; **BA3:** C13–N1–N2, C13–N5–N4, C13–N5–N6, C13–N9–N8, C13–N9–N10, C13–N1–N12; **BA4:** N1–C13–N5, N5–C13–N9, N9–C13–N1. The bond lengths of the tri-s-tetrazines and their corresponding monovalent cations are listed in Table 1.

3.1. Geometrical structures

For neutral species, the bond lengths in **BS1** range from 1.299 to 1.303 Å. All the lengths are slightly longer than that of a normal N=N double bond (1.25 Å), [17] and much shorter than that of a normal N–N single bond (1.45 Å) [17]. These results indicate that the bonds in **BS1** have considerable double bond character. The bond lengths in **BS2** range from 1.327 to 1.351 Å, which are slightly longer than that of a normal C=N double bond (1.29 Å), and shorter than that of a normal C–N single bond (1.47 Å). So, the bonds in **BS2** are nearly double bonds. From Fig. 1, one can find that the bonds in sets **BS1** and **BS2** are on the periphery of the three fused rings and these 12 bonds are essentially coplanar. That is to say, there is extensive conjugation around the periphery of the three fused rings in each neutral species. The bond lengths in set **BS3** range from 1.519 to 1.544 Å. These bonds are even longer than a normal C–N single bond. So, we may conclude that bonds in **BS3** are single bonds. All the three bonds in **BS3** are connected to the central carbon atom C13. Geometrical structures show that the central carbon C13 is at the pyramidal vertex and is not coplanar with the other atoms in the framework.

The structure of each monovalent cation is similar to its corresponding neutral species, except when R is N=NH, which

Table 1

Bond lengths (in Å) of the 11 carbon-centered tri-s-tetrazines, C$_4$N$_9$–R$_3$, and their corresponding monovalent cations optimized at the B3LYP/cc-pVDZ level

R	Neutral			Cation			R$_{cation–neutral}$		
	BS1	**BS2**	**BS3**	**BS1**	**BS2**	**BS3**	**BS1**	**BS2**	**BS3**
H	1.303	1.339	1.535	1.312	1.341	1.434	0.009	0.002	−0.101
OH	1.302	1.336	1.543	1.305	1.345	1.445	0.003	0.009	−0.098
F	1.303	1.328	1.543	1.309	1.336	1.440	0.006	0.008	−0.103
C≡N	1.299	1.327	1.541	1.309	1.350	1.431	0.010	0.023	−0.110
N$_3$	1.299	1.344	1.531	1.302	1.355	1.442	0.003	0.011	−0.089
NH$_2$	1.305	1.344	1.542	1.309	1.356	1.452	0.004	0.012	−0.090
NO$_2$	1.301	1.331	1.526	1.312	1.332	1.434	0.011	0.001	−0.092
N=NH	1.300	1.345	1.519	1.306	1.346	1.434	0.006	0.001	−0.085
N$_2$H$_3$	1.303	1.346	1.544	1.302	1.358	1.456	−0.001	0.012	−0.088
C≡CH	1.301	1.351	1.521	1.309	1.356	1.433	0.008	0.005	−0.088
CH=CH$_2$	1.301	1.351	1.521	1.309	1.356	1.434	0.008	0.005	−0.087

BS1, **BS2** and **BS3**: see text.

has its central carbon atom C13 nearly coplanar with the peripheral atoms. The remaining species, either neutrals or cations, are all pyramidal, looking like straw–hats. Compared to the corresponding neutrals, the bonds in the periphery of the three rings of the cations are elongated, while the bonds linked to the central carbon atom C13 are shortened. In addition, all the cations become flatter. As a result, the bond lengths of the cations become more "homogenized," when compared with those of the corresponding neutrals. In order to establish a trend, we also studied the divalent cation $C_4N_9H_3^{2+}$ by optimizing its structure at B3LYP/cc-pVDZ level. We find that the divalent cation $C_4N_9H_3^{2+}$ is even flatter than $C_4N_9H_3^+$, nearly coplanar. The C–N bond lengths in the divalent cation are almost the same, 1.344 Å in **BS2** set and 1.367 Å in **BS3** set. Furthermore, the pyramidal angles at C13 in **BA4** (Table 2) are compared with those in **BA1**–**BA3**. In tri-s-tetrazine, the pyramidal angles in **BA4** are about 102.6° for the neutral $C_4N_9H_3$, about 113.4° for $C_4N_9H_3^{1+}$ and about 120.0° for $C_4N_9H_3^{2+}$, while, for the monocations, they are between 115° and 122° in sets **BA1**–**BA3**. Obviously, the bulge at C13 in neutral species $C_4N_9H_3$ essentially disappears in $C_4N_9H_3^{2+}$. Similar results are found for the substituted species. It is noted that there is an important change in **BS3** (about 0.1 Å) when an electron is removed from the neutral. This implies the bonds linked to the central carbon atom C13 have gained significant double bond character upon the formation of the monovalent cation.

3.2. NBO analysis

An NBO analysis based on the structures optimized at the RB3LYP/cc-pVDZ level was carried out for all the neutrals. Results indicate that bonds N1–N12, N2–C3, N4–N5, N6–C7, N8–N9 and N10–C11 are identified as double bonds, while the remaining bonds are single bonds. By considering resonance structure, the N1–N2, C3–N4, N5–N6, C7–N8, N9–N10 and C11–N12 have double bond character. In other words, there are six double bonds and the six single bonds on the periphery of the species in an alternative pattern. NBO analysis also indicates that the π electrons are partially delocalized. For example, the electron occupancies of π_{N-N} and π_{C-N} of the

Table 2
The pyramidal angles at C13 in **BA4** (in degrees) of the 11 carbon-centered tri-s-tetrazines, and their corresponding monovalent and divalent cations optimized at the restricted/unrestricted B3LYP/cc-pVDZ levels

R	Neutral	Monovalent	Divalent
H	102.6	113.4	120.0
OH	101.6	111.5	120.0
F	101.8	112.3	120.0
C≡N	103.6	113.6	120.0
N_3	102.7	111.9	120.0
NH_2	101.5	110.7	120.0
NO_2	103.3	113.8	120.0
N=NH	103.5	113.0	120.0
N_2H_3	101.6	110.4	120.0
C≡CH	103.4	113.0	120.0
CH=CH$_2$	103.3	112.6	120.0

neutral species are 1.85 and 1.72, respectively. The delocalized electron numbers in π_{N-N} and π_{C-N} orbitals are 0.15 and 0.28, respectively. Owing to the delocalization of electrons in the π orbitals and the suitable orbital orientation, these bonds form an extensive conjugated π system. Our NBO analysis also shows that in each neutral species, atoms N2, N4, N6, N8, N10, N12 and C13 possess one lone pair, while N1, N5 and N9 have none. The electron occupancies are 1.90 in the lone pair orbitals of N2, N4, N6, N8, N10 and N12, 1.85 in the lone pair orbital of C13. This result indicates that the lone pair of C13 participates in the aforementioned extensive conjugated π system.

3.3. VB analysis

As discussed above, the 12 bonds on the periphery form a conjugated π system. This can be verified by the bond angles of sets **BA1**–**BA3**, and by the p- to s-character ratios (i.e., hybridization) of the atoms on the periphery. The bond angles in **BA1**–**BA3** are between 115° and 122°. The p- to s-character ratios of these atoms are between 1.7 and 2.1 for the σ bonding orbitals, and nearly pure p-character for the π bonding orbitals. Both of these results imply that these bonds are composed of sp^2 hybrid orbitals. On the other hand, all the pyramidal angles at C13 in **BA4**, N1–C13–N5, N1–C13–N9 and N5–C13–N9, are about 102.5°, which indicates that hybridization on C13 is close to sp^3. According to NBO analysis, the p- to s-character ratio for C13 in each bonding orbital is about 4.7. Our study shows that C13 also participates in the conjugated π system with its sp^3 hybrid orbital. That is, all atoms other than hydrogen in the neutral species participate in conjugated π system.

If the C13 does not participate in the conjugated π system, the molecule will have two unpaired electrons. One is located at C13, and the other may be delocalized among the peripheral atoms, thus forming a diradical. By taking the parent tri-s-tetrazine as an example, we attempted to optimize the structure of the supposed diradical at the UB3LYP/cc-pVDZ level. However, we failed to obtain convergence. The fact that an sp^3 hybrid orbital of central carbon atom C13 is a participant of the conjugated π system can be further confirmed by the electron density distributions of orbital #29, which is the extensive π bonding orbital (Figs. 2 and 3). The electron density contributions of all atomic orbitals in tri-s-tetrazine to molecular orbital #29 are listed in Table 3.

The total electron density in orbital #29 is 0.441. Each atom in sets **AS1**–**AS4** contributes 0.073, 0.021, 0.016 and 0.029, respectively, to the total electron density. That is, the contribution of C13 to the electron density of orbital #29 is 0.029. This value is even larger than that of the carbon atoms in set **AS3**, 0.023, indicating that the contribution of C13 to the conjugated π system exceeds those of other carbon atoms in the neutral species. The contribution of C13 to the conjugated π system can also be observed from the electron density maps of the orbital. Without the contribution of C13, the electron density map of orbital #29 is relatively flat (see top of Fig. 2). When the contribution of C13 is included, there is a significant concentration of electron charge above the center of the system
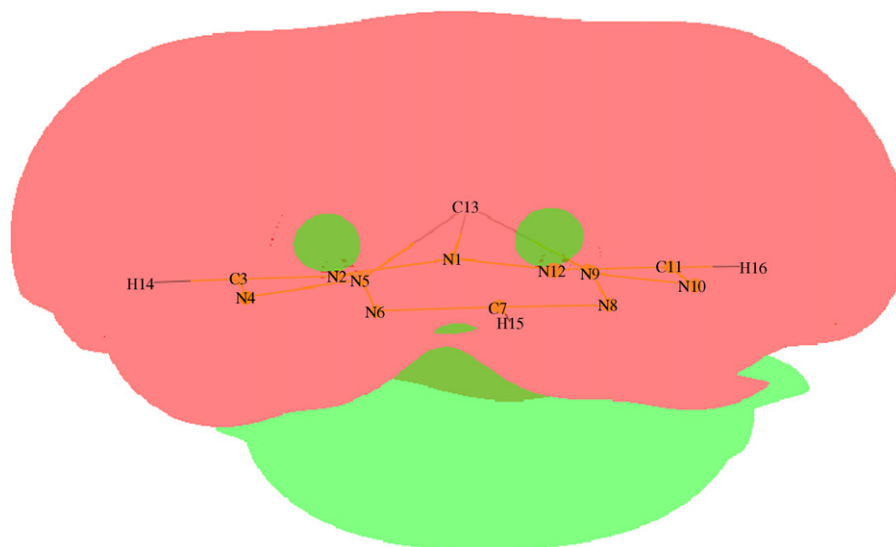
Fig. 2. Electron density map of orbital #29 of C_4N_9–H_3, without the participation of C13.

(see the upper midsection of Fig. 3). The contribution of atom C13 to the orbital #29 can be observed clearer from Fig. 4. Thus, we conclude that central atom C13 is a participant of the conjugated π system with its sp^3 hybrid orbital. Our NBO analysis shows that there is a lone pair on C13, and there exists considerable interaction (stabilizing energy $E(2)$ = 10.4 kcal mol^{-1}) between the lone pair and anti-bonding π^* orbitals of N1=N2, N5=N6 and N9=N10. This $E(2)$ is the largest stabilizing energy among all the interactions involving orbital #29. As is known, this donor (lone pair)–acceptor (π^*) interaction is the delocalization tendency of the donor electrons. The larger the $E(2)$, the higher the delocalization tendency. So, we can say conclusively that atom C13 participates in the conjugated π system with its lone pair.

The electron arrangement of the valence orbitals of C13 is shown in Scheme 1(a), where the hybrids participating in bonding with other atoms are enclosed in a dotted line box (this is also applied to the remaining schemes shown). Based on the NBO results presented above, the actual situation is closer to Scheme 1(b), with an additional electron on the hybrid orbitals. Where does this electron come from? To answer this question, it is helpful to analyze the hybrid orbitals of the peripheral atoms of the rings. All the three peripheral carbon atoms C3, C7 and C11 are sp^2 hybridized. The electron arrangements of these three atoms are shown in Scheme 1(c). All the nine nitrogen atoms are also sp^2 hybridized. Among them, nitrogen atoms N2, N4, N6, N8, N10 and N12 adopt the so-called "non-equivalent hybrid orbital" scheme: the lone pairs are located in
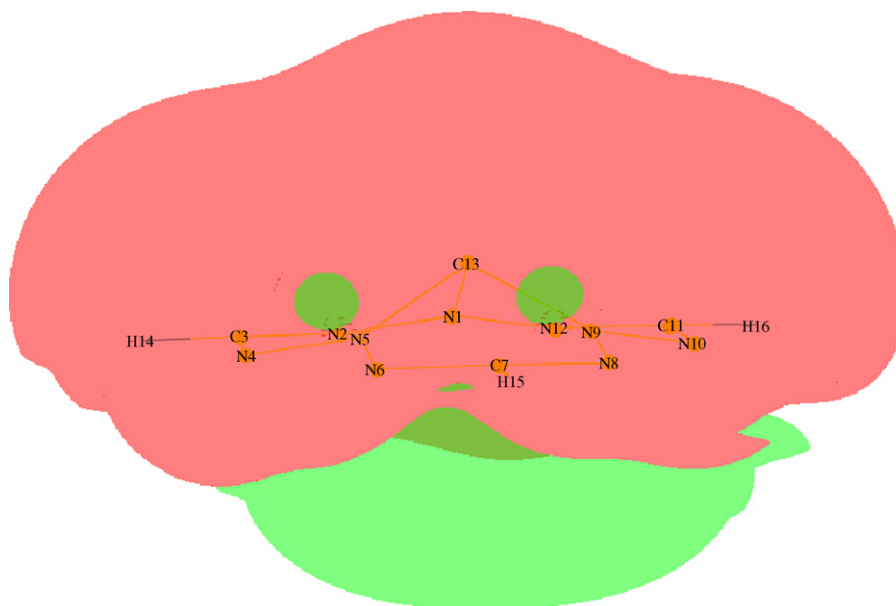

Fig. 3. Electron density map of orbital #29 of C_4N_9–H_3, with the participation of C13.

Table 3
Electron density distributions of the HOMO (orbital #45) of tri-s-tetrazine, C_4N_9–H_3

#45	AS1	AS2	AS3	AS4
1S	0.001	0.000	0.000	0.007
2S	0.005	0.000	0.000	0.037
3S	0.009	0.001	0.003	0.203
4PX	0.001	0.000	0.000	0.000
4PY	0.000	0.001	0.000	0.000
4PZ	0.046	0.000	0.039	0.127
5PX	0.000	0.000	0.000	0.000
5PY	0.000	0.000	0.001	0.000
5PZ	0.030	0.001	0.031	0.073
6D0	0.000	0.000	0.000	0.000
6D + 1	0.000	0.000	0.000	0.000
6D − 1	0.000	0.000	0.000	0.000
6D + 2	0.000	0.000	0.000	0.000
6D − 2	0.000	0.000	0.000	0.000
Sum	0.092	0.003	0.074	0.447
Total	0.276	0.019	0.222	0.447

AS1, **AS2**, **AS3** and **AS4**: see text.
Orbitals in the first column are the basis functions.
Sum: the contribution of each atom to orbital #45.
Total: the contribution of each set of atoms to orbital #45.

one of the sp^2 hybrid orbitals (Scheme 1(d)) and they do not participate in the conjugation. As expected, no lone pair is found on N1, N5 and N9, according to NBO analysis. Instead, these atoms are supposed to adopt the so-called "equivalent hybrid orbital" scheme: the electron pair does not take part in the hybridization, and it participates in the conjugation (Scheme 1(e)). Thus, the conjugated π system of the periphery of the rings contains 3 (C) + 9 (N) = 12 atoms. Atoms C3, C7, C11, N2, N4, N6, N8, N10 and N12 contribute 1 electron each, and atoms N1, N5 and N9 contribute 2 electrons each, totaling 15 electrons in all. This extensive conjugate π system is denoted as $_{12}\pi^{15}$, indicating that there is an unpaired electron system. If this unpaired electron and the unpaired electron in

the sp^3 hybrid orbital of C13 (Scheme 1(a)) combine to form a diradical, the resultant species would be highly unstable.

Since the number of electrons of the aforementioned $_{12}\pi^{15}$ system exceeds the number of atom centers, it is not a perfect conjugated π system since some electrons will occupy the less stable antibonding orbitals. On the other hand, the sp^3 hybrid orbital on C13 with only one unpaired electron is available for occupancy. Hence, one of the three excessive electrons in the $_{12}\pi^{15}$ system tends to fill in this sp^3 orbital to form an electron pair. According to the electron density of the HOMO, which is orbital #45, as listed in Table 3, the biggest contributor is the s and p electrons of atom C13 (0.477 out of the total electron density of 0.966), as expected. The other major components are mainly the s and p orbitals of N1, N5 and N9. From Table 3, one can find that the contribution of each atom in **AS1** to the HOMO (0.092) is much greater than that in **AS2** (0.003) and in **AS3** (0.074). The contributions of N1, N5, N9 and C13 to electron density of HOMO are shown in Fig. 5. Thus, a conjugated π system with 13 atoms and 16 electrons (denoted by $_{13}\pi^{16}$) is formed. The remaining two excessive electrons in the original $_{12}\pi^{15}$ system occupy the π^* orbital #44. It is clear that the electron topology of $_{13}\pi^{16}$ is far more stable than the aforementioned diradical.

Furthermore, NBO analysis shows that each of the species contains seven lone pairs, located at N2, N4, N6, N8, N10 and C13, respectively. By taking tri-s-tetrazine as an example, the orbital occupancies are 1.901 (ideally it should be 2.0) for each of the six nitrogen atoms, and 1.852 for C13. These (less than 2.0) occupancies imply that the lone pairs are delocalized and, as a result, the p-character of the N1–C13, N5–C13 and N9–C13 bonding orbitals increase remarkably. The p- to s-character ratios are 1.90 for N1, N5 and N9, which is close to the ideal value of 2.0 for sp^2. The corresponding ratio for C13 is 4.75, which far exceeds the idealized values of 3.0 for sp^3. Meanwhile, the corresponding ratios of the seven lone pairs are: 1.67 (instead of the ideal value of 2.0 for sp^2) for atoms N2, N4, N6, N8, N10 and N12; 1.08 for C13. These low ratios
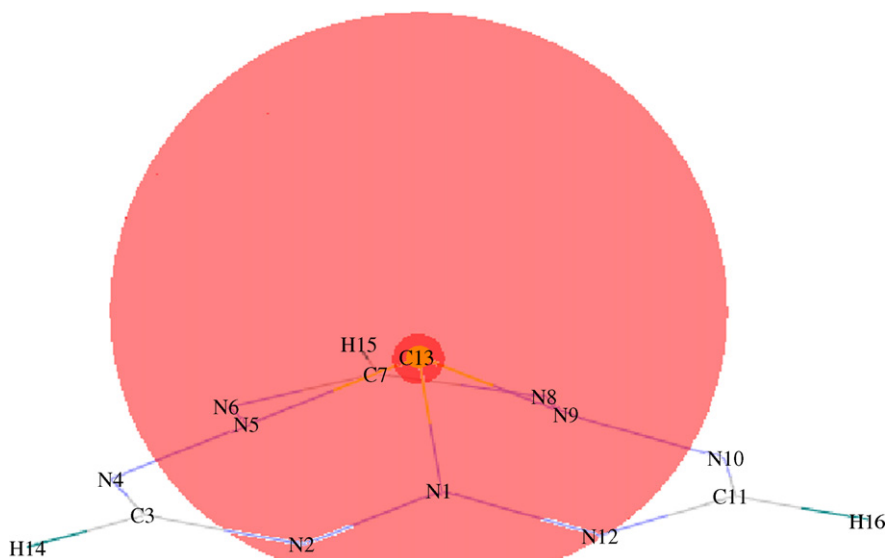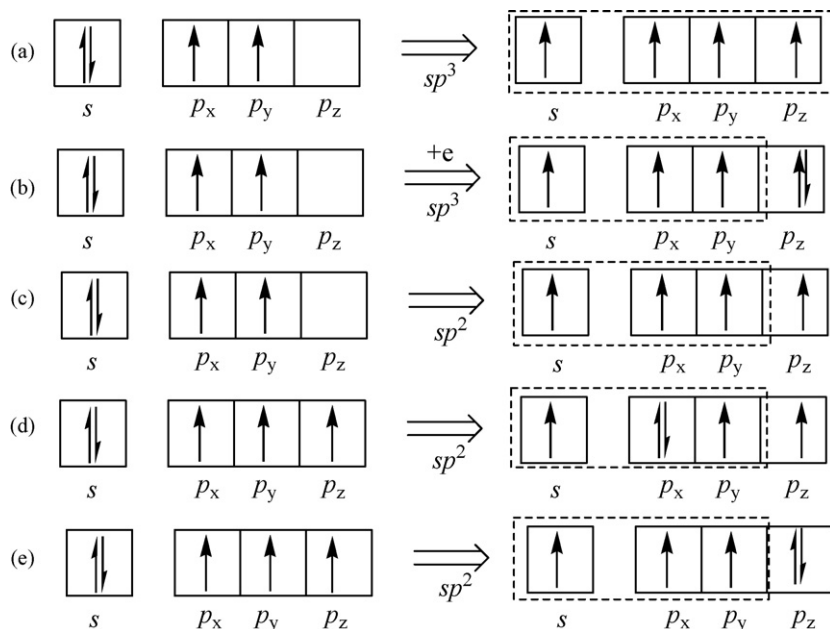

Fig. 4. The contribution of central carbon atom C13 to orbital #29 of C_4N_9–H_3.

Scheme 1. The hybridization schemes of different types of atoms in the tri-*s*-tetrazines.

indicate that the lone pairs are partially delocalized. All these results show that there exists a conjugated π system in each species covering the three rings, and the central carbon atom C13 participates in the conjugation with its lone pair in the sp^3 hybrid orbital. To conclude, the conjugated π effect is a predominant stabilizing factor for carbon-centered tri-*s*-tetrazine and its derivatives.

3.4. AIM analysis

Applying the AIM partitioning technique, a molecule is divided into non-overlapping atoms. Hence, molecular property is simply the sum of the individual atomic properties. It is noted that the proposed partitioning occurs in real space, consistent with successful and practically useful AIM concepts such as AIM distributed polarizabilities, dispersion coefficients and bond orders [48]. The value of electron density ρ over the interatomic surface (referred to as IAS ρ) between an atom pair acts as a bond order, which is defined as the integral values over the basins of the exchange correlation part of the two-particle density matrix $F(\Omega, \Omega')$ [49,50]. Another more rigorous physical interpretation (delocalization indexes) proposed by Fradera et al. [51] is now generally acknowledged. Theoretical index of the degree of bonding (i.e., bond order) between two
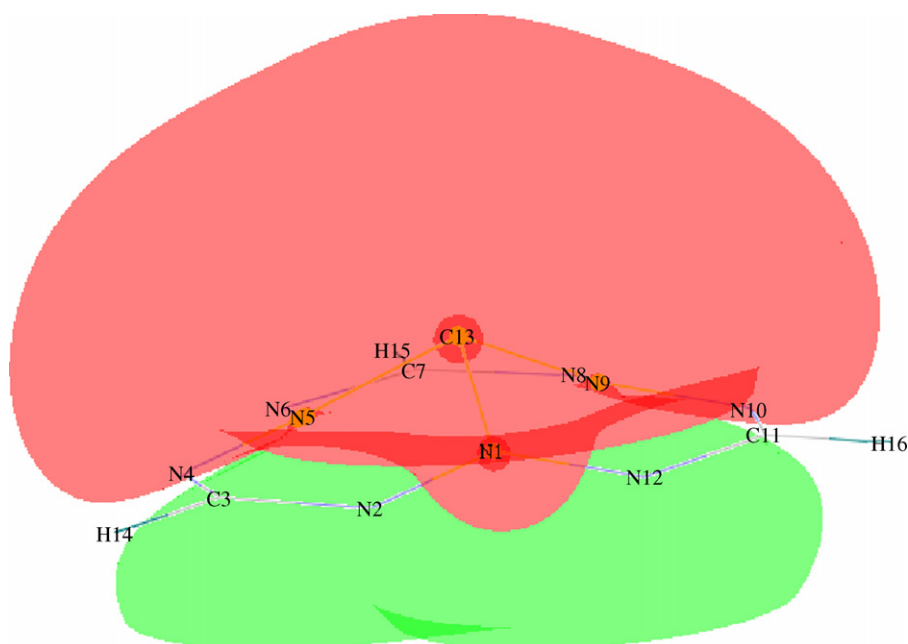

Fig. 5. The contributions of atoms N1, N5 N9 and central carbon atom C13 to orbital #45 of tri-*s*-tetrazine, C_3N_9–H_3.

Table 4
The IAS ρ-values of carbon-centered tri-s-tetrazines

R	Neutral			Cation			$\Delta_{Cation-neutral}$		
	BS1	**BS2**	**BS3**	**BS1**	**BS2**	**BS3**	**BS1**	**BS2**	**BS3**
H	1.540	1.429	1.072	1.497	1.401	1.194	−0.043	−0.028	0.122
OH	1.545	1.446	1.065	1.525	1.340	1.188	−0.020	−0.106	0.123
F	1.539	1.464	1.061	1.505	1.424	1.189	−0.034	−0.040	0.128
C≡N	1.546	1.430	1.089	1.503	1.404	1.199	−0.043	−0.026	0.110
N_3	1.554	1.439	1.079	1.533	1.397	1.192	−0.021	−0.042	0.113
NH_2	1.540	1.449	1.068	1.528	1.399	1.180	−0.012	−0.050	0.112
N=NH	1.549	1.439	1.096	1.515	1.415	1.199	−0.034	−0.024	0.103
N_2H_3	1.547	1.446	1.063	1.539	1.397	1.175	−0.008	−0.049	0.112
C≡CH	1.547	1.425	1.093	1.511	1.396	1.203	−0.036	−0.029	0.110
CH=CH_2	1.547	1.437	1.094	1.512	1.409	1.203	−0.035	−0.028	0.109

BS1, **BS2** and **BS3**: see text.

atoms only relative to that of a single bond, i.e., the index of multiple bonds is not considered. In molecular orbital theory, bond order is the sum of the products of the corresponding atomic orbital coefficients (weights) over all the occupied molecular spin-orbitals. Clearly the latter case is more universal. This indicates that IAS ρ-value between an atoms pair is equivalent to its bond order. A large IAS ρ-value implies a strong covalent bond. If the IAS ρ-value is greater than 1.0, the bond either is said to possess double bond properties. The IAS ρ-values of the 11 species and their corresponding monovalent cations are listed in Table 4. Indeed, AIM analysis shows that the framework of each species contains 15 BCPs. All the $\nabla^2\rho$-values of the BCPs are negative.

From Table 4, it can be found that all the IAS ρ-values are greater than 1.0, indicating that the bonds are covalent. The IAS ρ-values of bonds in sets **BS1** and **BS2** are about 1.5, which is very close to the IAS ρ-values of benzene (also about 1.5). Obviously, they have double bond character, as indicated by the results of NBO analysis. The IAS ρ-values of bonds in **BS3** range from 1.061 to 1.096, indicating that these bonds possess a small amount of double bond character. Though these values are only slightly greater than 1.0, these bonds do contribute to the conjugated π system. Hence, the previous conclusion that all atoms in the framework participate in the conjugated π system is further confirmed.

Compared to the neutral species, the IAS ρ-values of bonds in **BS1** and **BS2** in the cations decrease slightly, while those bonds in **BS3** increase markedly. These results indicate that the bonds on the framework tend to be homogenized after the neutrals are ionized. As discussed above, the divalent cation $C_4N_9H_3{}^{2+}$ is essentially coplanar. The IAS ρ-value is 1.43 for all the bonds in the framework.

3.5. Atomic charges

According to Bader's AIM theory [41], a molecule can be partitioned into atomic volumes. Within these volumes, an atomic charge takes on a value that is well defined by quantum mechanics, if it is integrated over these atomic subvolumes [52]. This leads to an unambiguous charge partition over the atoms composing a chemical system. The atomic charges of each atom

sets of the neutral species in this study are listed in Table 5. From this table, one can find that the AIM atomic charges (for neutrals only) range from −0.150 (R = NO_2) to −0.197 (R = H) for **AS1** atoms, −0.402 to −0.498 for **AS2** atoms. The atoms in sets **AS1** and **AS2** are all nitrogen which lie on the peripheries of the framework. However, the electron densities are quite different between the atoms in the two sets. Clearly, the atoms in **AS2** are more electronegative than those in **AS1**. For atoms in set **AS3**, the AIM atomic charges range from 1.046 (R = CH=CH_2) to 1.708 (R = F). For those in **AS4**, they range from 0.575 (R = N_2H_3) to 0.644 (R = C≡N). The atoms in **AS3** and **AS4** are all carbon. It is noted that substituents lead to a very wide range of atomic charges in **AS3**. The atoms in **AS3** are quite electropositive (more than 1.0), irrespective of electron-donating (e.g., C≡CH) or electron-withdrawing (e.g., F) substituents. According to Bader's partitioning, the atomic charges are not less than 1.0 for carbon atoms in these species, if the substitution effect is neglected. The central carbon atom C13 (i.e., the atom in **AS4**) is scarcely affected by the substituents and its atomic charge is unusually low (about 0.6). This low value is likely due to the following reason. Since the three nitrogen atoms linked to the central carbon atom are less electronegative, there is considerable electron transfer from these nitrogen atoms in **BS1** to the central carbon atom. This electron transfer leads to novel chemical properties for these species. When electrons gather at the central carbon atom C13, the species becomes carbanion-like. Since the AIM results are not highly sensitive to the basis set used in the calculation [53,54], the atomic charges obtained by this method are reliable.

Though the atomic charges obtained from NBO analysis are less reliable [54], they can still be used to predict the tendency of electron transfer. These atomic charges of the neutral and cationic species are listed in Table 6. It can be found that the nitrogen atoms in sets **AS1** and **AS2** are electronegative, while carbon atoms in sets **AS3** and **AS4** are electropositive, except when R = C≡CH, the charge is −0.075. The NBO atomic charges (for neutrals only) range from −0.022 (R = CH=CH_2) to −0.046 (R = F) for **AS1** atoms, −0.050 (R = NO_2) to −0.148 (R = C≡N) for **AS2** atoms, 0.138 (R = H) to 0.288 (R = NO_2) for **AS3** atoms (except R = C≡CH), 0.092 (R = NH_2) to 0.139 (R = N=NH) for **AS4** atoms. It can be seen that the NBO atomic charge distributions are similar to those of the AIM atomic

Table 5
Atomic charges (AIM charge or Bader charge) of carbon-centered tri-s-tetrazines, C_4N_9–R_3, and their, corresponding monovalent cations

R	Neutral				Cation				$\Delta_{Cation-neutral}$			
	AS1	AS2	AS3	AS4	AS1	AS2	AS3	AS4	AS1	AS2	AS3	AS4
H	−0.197	−0.498	1.108	0.587	−0.192	−0.382	1.143	1.016	0.005	0.116	0.035	0.429
OH	−0.174	−0.484	1.682	0.582	−0.148	−0.347	1.772	0.973	0.026	0.137	0.090	0.391
F	−0.165	−0.470	1.708	0.585	−0.139	−0.316	1.803	1.004	0.026	0.154	0.095	0.419
C≡N	−0.172	−0.412	1.154	0.644	−0.142	−0.284	1.230	1.058	0.030	0.128	0.076	0.414
N_3	−0.155	−0.418	1.520	0.612	−0.117	−0.292	1.590	0.988	0.038	0.126	0.070	0.376
NH_2	−0.183	−0.495	1.529	0.576	−0.140	−0.375	1.464	0.926	0.043	0.120	0.117	0.350
NO_2	−0.150	−0.402	1.406	0.643	−0.109	−0.287	1.448	1.061	0.041	0.115	0.042	0.418
N=NH	−0.170	−0.433	1.409	0.644	−0.146	−0.320	1.486	1.038	0.024	0.113	0.077	0.394
N_2H_3	−0.162	−0.495	1.512	0.575	−0.120	−0.357	1.598	0.913	0.042	0.138	0.086	0.338
C≡CH	−0.180	−0.447	1.122	0.632	−0.154	−0.323	1.158	1.030	0.026	0.124	0.036	0.398
CH=CH_2	−0.177	−0.472	1.046	0.632	−0.138	−0.346	1.067	1.006	0.039	0.126	0.021	0.374

charges. The NBO atomic charge distributions also suggest that there is electron transfer from the three nitrogen atoms, which link to C13, to the central carbon atoms.

3.6. The reaction centre

As discussed above, there is charge accumulation on the central carbon atom in each species. If that is the case, the central carbon atom C13 should be the reactivity center. This can be verified by the changes on every atom in the species upon ionization. It is known that there is charge redistribution when a neutral is ionized. The atom whose charge changes most should be the reactivity center. So, for the monovalent cations, we also carried out geometry optimization, vibrational frequency calculation, as well as AIM and NBO analyses. It is found that the monovalent cations retain the pyramidal structure of the neutrals. The AIM and NBO atomic charges of every atom set in each cation are listed in Tables 5 and 6, respectively. One can find that, for the cations, the nitrogen atoms in sets AS1 and AS2 bear negative charges, carbon atoms in sets AS3 and AS4 bear positive charges, in both AIM and NBO analyses. The atomic charge changes upon ionization of each sets are also listed in Tables 5 (AIM) and 6 (NBO). From Table 5, it can be seen that the negative charge of the nitrogens decrease, and the

positive charge of the carbons increase upon single ionization. The charge changes range from 0.005 (R = H) to 0.043 (R = NH_2) for the atoms in AS1, 0.113 (R = N=NH) to 0.154 (R = F) for the AS2 set, 0.021 (R = CH=CH_2) to 0.095 (R = F) for the atoms in AS3, 0.338 (R = N_2H_3) to 0.429 (R = H) for the atoms in AS4. These results show that there is very little electron redistribution for atoms in AS1 and AS3. That is, an electrophile will not attack any of these atoms. On the other hand, the charges of atoms in AS2 and AS4 change considerably, indicating that an electrophile should choose to attack these centers. More specifically, an electrophile should prefer to attack the atom in AS4 (i.e., the central carbon atom C13 in each species) because its charge changes most among the atoms in each species. Thus, we can conclude that the central carbon atom C13 in each species is the electrophilic reaction center. This finding can also be confirmed by the changes of NBO atomic charges. From Table 6, it can be seen that the charge changes range from 0.003 (absolute value for R = OH) to 0.025 (absolute value for R = NO_2) for the atoms in AS1, 0.023 (R = N_2H_3) to 0.053 (R = H) for the atoms in AS2, 0.025 (R = C≡CH) to 0.068 (R = F) for the atoms in AS3, 0.225 (R = NH_2) to 0.330 (R = H) for the atoms in AS4. The changes of the atoms in AS1–AS3 are negligible. The large charge change for the atoms in AS4 indicates that, once again,

Table 6
Net natural atomic charges (NBO charge or Mulliken charge) of carbon-centered tri-s-tetrazines, C_4N_9–R_3, and their corresponding monovalent cations

R	Neutral				Cation				$\Delta_{Cation-neutral}$			
	AS1	AS2	AS3	AS4	AS1	AS2	AS3	AS4	AS1	AS2	AS3	AS4
H	−0.038	−0.090	0.138	0.104	−0.056	−0.037	0.203	0.433	−0.017	0.053	0.065	0.330
OH	−0.040	−0.103	0.233	0.094	−0.043	−0.062	0.289	0.365	−0.003	0.041	0.056	0.271
F	−0.046	−0.080	0.280	0.109	−0.057	−0.034	0.347	0.416	−0.011	0.046	0.068	0.308
C≡N	−0.036	−0.079	0.182	0.150	−0.056	−0.036	0.231	0.456	−0.020	0.043	0.048	0.306
N_3	−0.033	−0.101	0.267	0.117	−0.038	−0.074	0.320	0.364	−0.005	0.028	0.054	0.248
NH_2	−0.032	−0.142	0.173	0.092	−0.028	−0.118	0.232	0.316	0.004	0.024	0.059	0.225
NO_2	−0.035	−0.050	0.288	0.157	−0.059	−0.007	0.338	0.472	−0.025	0.043	0.050	0.315
N=NH	−0.031	−0.081	0.237	0.139	−0.051	−0.045	0.301	0.427	−0.020	0.036	0.065	0.288
N_2H_3	−0.031	−0.148	0.243	0.092	−0.027	−0.125	0.298	0.306	0.004	0.023	0.055	0.214
C≡CH	−0.042	−0.096	−0.075	0.127	−0.055	−0.061	−0.050	0.401	−0.012	0.035	0.025	0.274
CH=CH_2	−0.022	−0.128	0.135	0.121	−0.031	−0.099	0.180	0.380	−0.008	0.029	0.045	0.259

AS1, AS2, AS3 and AS4: see text.

the central carbon atom C13 is the reactive center for the neuclophilic reactions of each species.

3.7. IEs and the reactivity centre

The central carbon atom C13 in each species is confirmed as the reactive center by the charge changes upon ionization. An ionization process may include two steps: first, one electron is removed from the central carbon atom, then, the charges are redistributed to reach an "equilibrium" state. That is, the ionization takes place at C13. In order to estimate the reactivity of the species, we carried out the IE calculations of processes $C(^3P)/C^+(^2P)$, $Al(^2P)/Al^+(^1S)$ and $C_2H_2/C_2H_2^+$, as well as those of tri-s-tetrazines. The calculated IEs at specified computational level and experimental IEs are listed in Table 7. It can be found that the calculated IEs are close to the available experimental data. This implies that, for comparison purposes, our calculated IEs are fairly reliable. The IEs of tri-s-tetrazines range from 5.38 to 8.55 eV at the B3LYP/cc-pVDZ level. These values are much lower than that of the $C(^3P)/C^+(^2P)$ (11.520 eV at the same computational level). As mentioned above, the ionized electron of each tri-s-tetrazines mainly comes from C13. As this electron from C13 can be removed easily, this atom should be the center of high reactivity.

3.8. Carbanion properties

A carbanion is a nucleophile. Structural study and VB analysis of the tri-s-tetrazines show that the central carbon atom C13 in each species receives an extra electron from the other atoms and this electron pairs with the single electron in C13's sp^3 hybrid orbital. AIM and NBO analyses indicate the positive charge on C13 in each species is much lower than those of the other carbon atoms in the same species. From the previous IE result and the AIM and NBO charge changes upon ionization

indicate that all the species are highly reactive, and the reaction center of each species is the central carbon atom C13. This carbon atom with low electropositivity and high reactivity suggests that the species possess carbanion character, even though there is no explicit negative charge on the carbon atom.

The stability and reactivity of a carbanion are determined by several factors [22–24], which include: (1) The inductive effect. Electronegative atoms/groups adjacent to the negative charge will stabilize the charge. As can be seen from Fig. 1, the electronegative atoms N1, N5 and N9 in each species are adjacent to the supposed charge-bearing atom C13. (2) Hybridization of the charge-bearing atom. The greater the s-character of the charge-bearing atom, the more stable the anion is. VB and NBO analyses show that the central carbon atom C13 bear less positive charge than the other carbon atoms in the species. The charge-bearing atom C13 is sp^3 hybridized. The s-character of the lone pair is considerably higher (Table 8). For all the species, the s-character of the lone pair orbital of C13 is nearly equal to the p-character: the p- to s-character ratios are 1.08, 0.98, 0.98, 1.20, 1.09, 0.99, 1.15, 1.24, 0.99, 1.20, 1.20 for R = OH, F, CN, N_3, NH_2, NO_2, N=NH, N_2H_3, C≡CH, and CH=CH$_2$, respectively. These small ratios indicate that the hybridization of charge-bearing atom has high s-character. So we may say that these species are carbanion-like. (3) The extent of conjugation of the anion. Resonance effects (conjugation) can stabilize the anion. As discussed above, there is a $_{12}\pi^{15}$ conjugated π system on the periphery of the rings. The unpaired electron in the sp^3 hybrid orbital of C13 contributes to this system and forms a $_{13}\pi^{16}$ system in the process. Such an extensive conjugation further stabilizes the carbanion-like molecule. The $p\pi$ conjugate effect can be measured by the stabilizing energies $E(2)$ in the NBO analysis (Table 8). The

Table 7
The total energies of neutral tri-s-tetrazines $E_{0,\text{Neutral}}$ (in au) and their corresponding monovalent cations $E_{0,\text{Cation}}$ (in au), and ionization energies IE (in eV) calculated at the B3LYP/cc-pVDZ level

R	$E_{0,\text{Neutral}}$	$E_{0,\text{Cation}}$	IE[a]	IE$_{\text{exp}}$
H	−646.65258	−646.39220	7.09	
OH	−872.33718	−872.10072	6.43	
F	−944.39221	−944.11580	7.52	
C≡N	−923.36445	−923.06051	8.27	
N$_3$	−1137.45506	−1137.21062	6.65	
NH$_2$	−812.70890	−812.51122	5.38	
NO$_2$	−1260.14576	−1259.83145	8.55	
N=NH	−974.98332	−974.72062	7.15	
N$_2$H$_3$	−978.61490	−978.41502	5.44	
C≡CH	−875.06259	−874.81075	6.85	
CH=CH$_2$	−878.78431	−878.54998	6.38	
Ethyne	−77.33323	−76.92494	11.11	11.04[b]
C	−37.85198	−37.42861	11.52	11.26[c]
Al	−242.38286	−242.16142	6.03	5.99[c]

[a] IE of ethyne calculated at B3LYP/cc-pVDZ level. IE $= E_{\text{ion}} - E_{\text{neutral}}$.
[b] Experimental IE of ethyne.
[c] E_{ion} and E_{neutral} are taken from http://chemistry.anl.gov/compmat/g3energies/G3atom.htm.

Table 8
The p- to s-character ratio of the lone pair orbital (sp^3 hybridized) of neutral tri-s-tetrazines and their corresponding monovalent cations and the stabilizing energy $E(2)$ (in kcal mol^{-1})

R	C13[a]	**AS2**[b]	**BS1**[c]	$^+$C13[d]	$E(2)$[e]
H	1.08	1.67	4.75	3.59	10.4
OH	0.98	1.70	5.03	2.81	8.8
F	0.98	1.64	5.03	3.09	9.2
C≡N	1.20	1.64	4.47	3.80	12.9
N$_3$	1.09	1.70	4.72	2.98	10.7
NH$_2$	0.99	1.71	4.99	2.55	8.7
NO$_2$	1.15	1.68	4.57	3.58	12.2
N=NH	1.24	1.67	4.39	3.54	12.8
N$_2$H$_3$	0.99	1.72	5.02	2.46	8.6
C≡CH	1.20	1.64	4.47	3.53	12.1
CH=CH$_2$	1.20	1.71	4.47	3.37	12.2

[a] The p- to s-character ratio of the lone pair orbital (sp^3 hybridized) of C13 (neutral).
[b] The p- to s-character ratio of the lone pair orbital (sp^2 hybridized) of atoms in **AS2** (neutral).
[c] The p- to s-character ratio of the bond orbitals (sp^3 hybridized) of C13 in **BS1** (neutral).
[d] The p- to s-character ratio of the lone pair orbital (sp^3 hybridized) of C13 (cation).
[e] It is noted that the $E(2)$ is $p\pi$ interaction energy, where the p comes from lone pair orbital (sp^3 hybridized) of C13 and π is one antibonding orbital of the moieties of N2⋯N1⋯N12, N4⋯N5⋯N6 and N8⋯N9⋯N10.

Table 9
The total energies E_0 (in au, including zero-point energy corrections) and the enthalpies H (in au, including zero-point energy corrections), the ΔH_f (in kcal mol^{-1}) of tri-*s*-tetrazines calculated at the RB3LYP/cc-pVDZ level

R	E_0	H_{298}	ΔH_f
H	−646.65258	−646.64361	273.3
OH	−872.33718	−872.32466	135.2
F	−944.39221	−944.38066	134.5
C≡N	−923.36445	−923.34980	394.5
N$_3$	−1137.45506	−1137.43766	482.7
NH$_2$	−812.70890	−812.69536	260.5
NO$_2$	−1260.14576	−1260.12851	263.9
N=NH	−974.98332	−974.96798	433.4
N$_2$H$_3$	−978.61490	−978.59721	341.8
C≡CH	−875.06259	−875.04702	461.0
CH=CH$_2$	−878.78431	−878.76807	311.7
TsTA[a]	−613.63168	−613.62290	102.9

[a] The reference molecule: nitrogen-centered tri-*s*-triazine.

$E(2)$ here is the $p\pi$ interaction energy, where the p comes from lone pair orbital (sp^3 hybridized) of C13 and π is an antibonding orbitals of the moieties of N2⋯N1⋯N12, N4⋯N5⋯N6 and N8⋯N9⋯N10. Among all the interactions, those between the lone pair from C13 and the aforementioned moieties are the largest in each species. The stabilizing energies $E(2)$ are 10.4, 8.8, 9.2, 12.9, 10.7, 8.7, 12.2, 12.8, 8.6, 12.1 and 12.2 kcal mol^{-1} for R = OH, F, CN, N$_3$, NH$_2$, NO$_2$, N=NH, N$_2$H$_3$, C≡CH, and CH=CH$_2$, respectively.

Thus, all our results indicate that 11 tri-*s*-tetrazines studied in this work have carbanion-like properties and they should be highly reactive with electrophiles. They are expected to have potential applications in the field of molecular materials, such as nanomaterials, and in the field of biochemistry, such as biomedicine.

3.9. Relative stabilities

The relative stabilities of molecules are usually estimated by their heats of formation (ΔH_f). In this study, we use nitrogen-centered tri-*s*-triazine as a reference, since it was synthesized in 2002 [16], and has been subjected to extensive theoretical studies in the past 3 years [17–21]. The ΔH_f values of the 11 species and the reference molecule are listed in Table 9. Of all the carbanion-like species, C$_4$N$_9$(OH)$_3$ and C$_4$N$_9$F$_3$ are the most stable species because their ΔH_f's are only 135.2 and 134.5 kcal mol^{-1}, respectively. These high ΔH_f values for the other tri-*s*-tetrazines suggest that they may be polynitrogen energetic materials.

4. Conclusions

We have applied NBO and AIM analyses as well as the VB theory to investigate the bonding patterns of carbon-centered tri-*s*-tetrazine and its 10 derivatives. Valence orbital analysis is presented to explain the pyramidal structure and the electron arrangement in the orbitals of these species. Some results have been obtained: (1) The atoms on the periphery of each species is sp^2 hybridized. Each of these 12 atoms offers an orbital to form an extensive conjugation system of the $_{12}\pi^{15}$ type. The central carbon atom C13 is sp^3 hybridized, which makes the molecule non-planar and shape like a straw–hat. Atom C13 also participates in the conjugated π system in a novel way with its fully occupied sp^3 hybridized orbital. Thus, an extensive conjugate system $_{13}\pi^{16}$ is formed covering the whole the framework. (2) From the AIM and NBO results, we find that the central carbon atom C13 has positive charge lower than those of the other carbon atoms. Thus, we predict atom C13 should be the attacking site for incoming electrophiles. That is, the species are carbanion-like. (3) The atomic charges undergo redistribution when the species is ionized. The atomic charge changes upon ionization suggest that the reactive center of the species is C13, as its charge change is the greatest among all the atoms. (4) All the species have low first IEs, which indicate that the species can lose an electron easily. The lost electron mainly comes from C13. So once again we can see that an electrophile prefers to attack atom C13. Based on thermochemical consideration, among the 11 molecules studied, carbon-centered tri-*s*-tetrazine halides (i.e., C$_4$N$_9$F$_3$) and hydroxide (i.e., C$_4$N$_9$(OH)$_3$) are most likely to be synthesized and separated. These molecules may have wide applications in organic chemistry, in organometallic chemistry and in alkyl lithium chemistry once they are synthesized.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.mgm.2007.05.004.

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