

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 (C₄N₉H₃), and its 10 derivatives (C₄N₉-R₃, where R = OH, F, CN, N₃, NH₂, NO₂, N=NH, N₂H₃, C≡CH, and CH=CH₂) 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 C₄N₉ 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 these 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 (C₄N₉H₃) (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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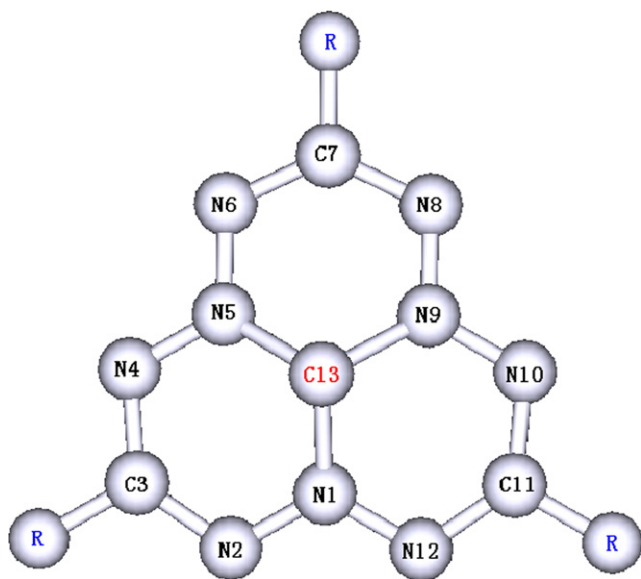


Fig. 1. The geometrical structure and atomic labeling of tri-*s*-tetrazine, where R = OH, F, CN, N₃, NH₂, NO₂, N=NH, N₂H₃, C≡CH, and CH=CH₂.

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, N₃, NH₂, NO₂, N=NH, N₂H₃, 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, C₄N₉H₃, 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 plane-1. 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 $\nabla\rho$ 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

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