International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2019): 7.583

# Charge Distribution and Ionization Potential of $N_8$ Isomers

**Eena Bahan**[1*], **R. S. Prasad**[2]

[1]Department of Physics S. C. E. Sasaram, India
[*]Email:14200shprateek[at]gmail.com
[2]Former Head Department of Physics, Magadh University, Bodh Gaya, India

**Abstract:** ***By use of an approximate self-Consistent Field (SCF) method MRINDO/S, the potential nitrogen molecules, octaazacubane$N_8$isomers were studied. The $N_8$ isomers considered in the present study belong to the molecular point groups $O_h$, $D_{2h}$ and $C_{2v}$ respectively. We report their charge distribution and ionization potential of the $N_8$ isomers. The charge distribution was accounted for by making use of Mulliken population analysis.***

**Keywords:** - $N_8$ isomers, Charge distribution and ionization potential

## 1.Introduction

Although cubane and cyclooctatetrane are known experimentally, unsubstituted pentalene has never been synthesized; nevertheless, the Vibrational analysis of Leininger et al. [1] indicates that the three nitrogen analogues namely octaazacubane of $O_h$ symmetry, an all - nitrogen analogue of cyclooctatetrane of $D_{2d}$ Symmetry and a planar bicyclic structure analogous to pentalene (octaazapentalene) of $D_{2h}$ symmetry represent potential energy minima, The $N_8$ isomers are metastable and the metastability of octaazapentalene is attributed to two π electrons present in it but not in pentalene, according to the rule of topological charge stabilization, Further, they concluded that since all three minima are very high - lying with respect to $4N_2$, their potential application is as high energy density materials (HEDMs).

Synthesis of the metastable molecules $N_4$, $N_6$ and $N_8$ would offer a potential route toward the storage of large amounts of energy. The evolving quest for more efficient explosives and rocket propellants has led to the examination of new and novel ways of storing energy [2]. A great deal of effort has been focused on increasing energy density by producing highly strained molecular systems, Strained hydrocarbons such as tetrahedrane and cubane have occupied the interest of researchers for many years [3]. One way of further increasing the energy of these systems is to replace CH fragment with an $N_2$ atom. In the limit of full replacement, nitrogen analogues of tetrahedrane and cubane are obtained. While one would expect these molecules to be metastable thermodynamically, pathways for decomposition to ground state N are forbidden by orbital symmetry. Therefore, it is possible that $N_4$ and $N_8$ can be observed experimentally.

The intense scientific and popular interest in the $C_{60}$ molecule has naturally raised the question whether other important cluster species have been systematically overlooked, N, clusters are reasonable candidates for the following two reasons. First, a number of $(CH)_n$, clusters have been synthesized, which are isoelectronic with $N_n$. It is possible that these nitrogen structures will show analogous stability. Second, $N_n$ clusters would be high energy density materials (HEDMs). The dissociation energy of $N_2$ (N ≡ N triple - bond energy) is 225 kcal/ mol, while the standard N = N double - bond energy is 100 kcal/mol and that of N - N single bond is 40 kcal/mol [4]. Since the N ≡ N triple - bond energy (225kcal/mol) is much more than three times the single - bond energy (3 x 40 = 120 Keal/mol), this suggests that the $N_n$, clusters with N - N single bonds may release sufficient amounts of energy when they dissociate into $N_2$molecules For instance, the cluster $N_{2n}$, Which has 3n single N - N bonds (each nitrogen atom connecting to three other nitrogen atoms with single bonds), will release as much as 225n -40 x 3n= 105n kcal/mol energy when it decomposes into $nN_2$; molecules. Also since the N = N double - bond energy (100 kcal/mol) is still larger than that of two single bonds (2 x 40 = 80 kcal/mol), the ideal HEDM candidates are those clusters containing N - N single bonds, This rough estimation of the decomposition energy may be compared with the results of recent high-level theoretical studies. For tetraazatetrahedrane $N_4$ (105 x 2 = 210 kcal/mol), the relative energy to $N_2$ was reported as 191 kcal/mol at the TZ2P CCSD level of theory [5] or 183 kcal/mol at the 6-311 + G(3df) Becke 3 LYP level [6]. For octaazacubane $N_8$ (105 x 4 = 420 kcal/mol), the analogous relative energy was reported as 450 (TZ2P CCSD)[5], 442 [6 - 311 + G (3df) Becke LYP] [6], or 423 kcal/mol [DZP CCSD (T)] [7], respectively.

As mentioned earlier, in 1995, Leininger et al. [1] investigated two new isomers of cubane namely an all-nitrogen analogue of cyclooctatetrane of $D_{2d}$ symmetry and octaazapentalene of $D_{2h}$, symmetry. By use of DZP basis set accompanied by the SCF, MP2, CISD, and CCSD methods they reported optimized geometries and harmonic vibrational frequencies of the two newly investigated isomers and also of the previously investigated structure octaazacubané of $O_h$ symmetry. High - quality estimates of the energy differences between these $N_8$ isomers and $4N_2$) were determined using the CCSD (T) method. In 1996, Gimarc and Zhao studied the strain energies and resonance energies of these three $N_8$ clusters using *ab iniotio* methods [7]. The nitrogen cluster strain energies are generally of the same order of magnitude as those of isostructural hydrocarbon clusters, and resonance energies of nitrogen clusters are much smaller than those of the comparable aromatic hydrocarbons. Recently, Glukhovtsev et al. [6]

investigated $N_n$, clusters more systematically. The number of the structures (including two saddle points) for $N_8$ clusters in their paper has reached as many as eight.

All the previously investigated $N_8$ clusters, except the cubic structure, contain N = N double bonds. For the purpose of searching for HEDM candidates, Tian et al. [8] wanted to limit their attention to isomers with only N - N single bonds. With the help of graph theory, they found two new previously uninvestigated isomers, which have only N - N single bonds. One has $D_{2h}$, symmetry, and the other, analogous to cuneane designated octaazacuneane, has $C_{2v}$, symmetry.

The above studies stimulated us to consider the $N_8$ clusters to account for their spectroscopic characteristics. In the present study we have considered three $N_8$ clusters; two of these octaazacubane and octaazacuneane contain only N - N single bonds while the third octaazapentalene contains N = N double bonds too.

## 2.Charge Distribution

The net charge distributions in the isomers are shown in Fig.1. We know according to the chemical intution that higher the electron density on N, the higher is its donor character. Due to increase in negative charge density on N, its size is slightly increased. If positive charge is developed on N, its donor character is diminished and hence its basic character is decreased, on this basis, all the nitrogen atoms in octaazacubane, except those numbered4, 5 and 7, exhibit donor character, On the other hand, fifty percent of the nitrogen atoms inoctaazapentalene and octaazacuneane exhibit donor character while the others behave like acceptors. Here we would like to mention about the magnitude of the charges developed on in the isomers. This is the little in octaazacubane while in the other two isomers this is too large; the charges developed on different nitrogen atoms in octaazapentalene are more thanten times that in octaazacuneane.

## 3.Lonization Potentials

The first ionization potential of octaazacubane is interpreted as the removal of a $\sigma$electronwhile the second as the removal of a $\pi$ one, looking at the values of these two ionization potentials we infer that both the $\pi$ and $\sigma$ electrons have the same probability to leave the molecule first. Prasad and Kumar [10] found approximately a similar situation inoctaazacubane - aside the reversal in the appearance of $\sigma$ and $\pi$ electrons. Besides, near constancy in the ionization potentials of octaazacubane makes it easy to infer that some of the excited states would show degeneracy. This is in consistent with the earlier study [10].On the other hand, the first removed electron in octaazapentalene and octaazacuneane is a$\pi$ electron while the second removed electron is a$\sigma$ one. In contrast to octaazacubane, the first two ionization potentials of octaazapentalene and octaazacuneane are not exactly the same but differ in magnitude and hence their spectra would be more structured than octaazacubane. This aspect of the spectra will be discussed in the succeeding section.

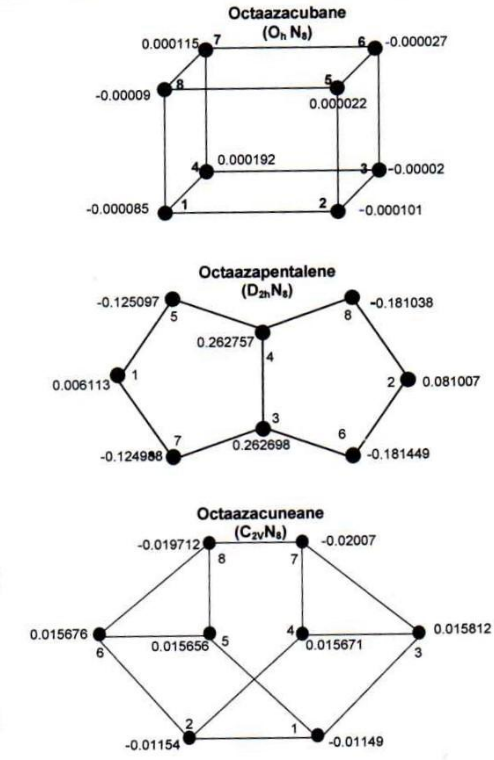
## 4.Results

Table 1 contains ionization potentials deduced from Koopmans theorem [9] and the corresponding orbital symmetries. The first columns of Table 1 contain ionization potentials and symmetries of the orbitals reported by Prasad and Kumar for octaazacubane only [10]. The Charge distribution is cited on page. No. 5.

**Table 1:** The lowest ionization potential of $N_8$ isomers

| Molecule (Symmetry) | Previous Work | | This Work | | |
|---|---|---|---|---|---|
| | I.P. | Type of orbital | I.P. | Sym. Of Orbital | Type of orbital |
| Octaaz-Acubana ($O_h$) | 11.197 | $t_{1g}$ $\pi$ | 10.819 | $a_{1g}$ | $\sigma$ |
| | 11.199 | $a_{2g}$ $\sigma$ | 10.819 | $t_{1g}$ | $\pi$ |
| | 13.027 | $t_{1u}\pi$ | 10.823 | $a_{2g}$ | $\sigma$ |
| | 13.040 | $a_{2u}\sigma$ | 12.934 | $t_{2g}$ | $\sigma$ |
| | 14.385 | $T_{2g}$ $\pi$ | 12.953 | $a_{2g}$ | $\sigma$ |
| Octa Azapentalene ($D_{2h}$) | | | 50.781 | $a_{1g}$ | $\sigma$ |
| | | | 10.635 | $a_u$ | $\pi$ |
| | | | 11.452 | $b_{1u}$ | $\sigma$ |
| | | | 11.918 | $b_{2u}$ | $\pi$ |
| | | | 12.157 | $b_{2g}$ | $\sigma$ |
| Octaazacuneane ($C_{2v}$) | | | 41.319 | $b_{1u}$ | $\sigma$ |
| | | | 46.831 | $a_g$ | $\sigma$ |
| | | | 11.031 | $a_2$ | |
| | | | 11.211 | $a_1$ | $\sigma$ |
| | | | 11.268 | $b_2$ | $\sigma$ |

Fig. 1 The net charge distribution in $N_8$ isomers. The spheres represent nitrogen atoms with their respective numbers



## References

[1] M L Leininger,C D Sherrill and H F Schaefer J, Phys. Chem. 99 2324 (1995)
[2] Proceedings of the High Energy Density Materials Contractor's Conferences 25 - 28 February 1990, Long beach CA
[3] A good review of strained organic compounds can be found in Chem. Rev. 5 89 (1989)
[4] J E Huheey, E A Keiter and R L Keiter Inorg. chem. 4" ed.; Harper-Collins College Publishers: New York 1993 p. A31
[5] W J Lauderdale, J F Stanton and R J Bartlett J. Phys. Chem. 96 1173 (1992)
[6] M N Glukhovtsev, H Jiao and P V R Schleyer Inorg. Chem. 35 7124 (1996)
[7] B M Gimarc and M Zhao Inorg. Chem. 35 3289 (1996)
[8] A Tian, F Ding, Zhang, Y Xie and H F Schaefer III J. Phys. Chem., 101 1946 (1997)
[9] T Koopmans Physica 1 104 (1933)
[10] R.S Prasad and K Kumar Indian J. Phys, 78 (12) 1391 (2004)