

## MRINDO/S-CI Calculation on the Electronic Spectra of N<sub>8</sub> Isomers

EENA BAHAN<sup>1\*</sup>, RAJ SHEKHAR PRASAD<sup>2</sup> AND R. S. PRASAD<sup>3</sup>

1. Department of Physics S. C. E. Sasaram, India
2. Department of Mathematics, Government Engineering College, Buxar, India
3. Former Head Department of Physics, Magadh University, Bodh Gaya.

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**Abstract:** MRINDO/S-CI Calculation Completed by singly excited configuration interaction was performed on the octaazacubane, octaazapentalene and octaazacuneane. The importance of outer (Rydberg) atomic orbitals is stressed and it is found that a few singlet-singlet transitions of the higher azines lead to an excited state with considerable Rydberg character.

**Keywords:** - MRINDO/S, octaazacubane, octaazapentalene and octaazacuneane.

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### I. 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<sub>h</sub> symmetry, an all —nitrogen analogue of cyclooctatetrane of D<sub>2d</sub> Symmetry and a planar bicyclic structure analogous to pentalene (octaazapentalene) of D<sub>2h</sub> symmetry represent potential energy minima, The N<sub>8</sub> 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<sub>2</sub>, their potential application is as high energy density materials (HEDMs).

Synthesis of the metastable molecules N<sub>4</sub>, N<sub>6</sub> and N<sub>8</sub> 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 tetrahydrane 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<sub>2</sub> atom. In the limit of full replacement, nitrogen analogues of tetrahydrane 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<sub>4</sub> and N<sub>8</sub> can be observed experimentally.

The intense scientific and popular interest in the C<sub>60</sub> molecule has naturally raised the question whether other important cluster species have been systematically overlooked, N<sub>n</sub> clusters are reasonable candidates for the following two reasons. First, a number of (CH)<sub>n</sub> clusters have been synthesized, which are isoelectronic with N<sub>n</sub>. It is possible that these nitrogen structures will show analogous stability. Second, N<sub>n</sub> clusters would be high energy density materials (HEDMs). The dissociation energy of N<sub>2</sub> (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 (225

kcal/mol) is much more than three times the single — bond energy (3 x 40 = 120 Keal/mol), this suggests that the N<sub>n</sub> clusters with N - N single bonds may release sufficient amounts of energy when they dissociate into N<sub>2</sub> molecules For instance, the cluster N<sub>2n</sub>, 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<sub>2</sub> 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 tetraazatetrahydrane N<sub>4</sub> (105 x 2 = 210 kcal/mol), the relative energy to N<sub>2</sub> 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<sub>8</sub> (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 octaazacubane 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 initio* 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.

## II. Geometry of the $N_8$ Isomers

The geometries of octaazacubane and octaazapentalene were taken from Leininger et al. [1] while the geometry of octaazacuneane was taken from Tian et al. [8]. Since the geometries of molecules play invaluable role in spectral calculations, we have used the above said geometries because these were optimized at the correlated level of theory.

## III. Singlet excitations

### 3.1 Octaazacubane

The lowest singlet excitation in octaazacubane is predicted at 6.296 eV. This does indicate that the octaazacubane spectrum cannot be expected in the visible or in the near-ultraviolet, for it appears in the medium ultraviolet under the approximation used in this work. This agrees with the previous prediction [10] but, in contrast, the lowest excitation ( $n \rightarrow \sigma^*$ ) is allowed ( $f = 0.0374$ ) while this was forbidden in Ref. [10]. The first absorption which concerns essentially the  $n \rightarrow \pi^*$  transition takes place at 6.321 eV and this transition is more intense ( $f = 0.0439$ ) than the lowest one. Several intense transitions are reported in the spectrum of octaazacubane but the most intense of all appears at 7.474 eV. This is an  $n \rightarrow \sigma^*$  transition with an oscillator strength amounting to 0.0782. This region of energy therefore corresponds to the maximum absorption region in octaazacubane. Of interest is the presence of an  $n \rightarrow \pi^*$  transition below the maximum absorption region. This  $n \rightarrow \pi^*$  transition exhibits an oscillator strength amounting to 0.0551, Thus these two transitions are of comparable intensity but they can be easily observed experimentally because the former is z-polarized while the latter is y-polarized, Comparing our results with the previous calculation [10] we notice that the present maximum absorption region in octaazacubane is shifted by about 1eV towards the shorter wavelength side of the spectrum.

The spectrum of octaazacubane consists of three closely spaced Rydberg excitations. All these transitions are  $n \rightarrow \sigma_R^*$  in character and appear at 6.953, 6.958 and 6.959 eV, respectively. The corresponding quantum defects of these Rydberg excitations are the same of magnitude 1.12. Obviously they form the members of ns Rydberg series. None of these transitions exhibits intensity and hence they cannot be observed experimentally without stable experimental conditions. According to the previous calculation [10] the spectrum of octaazacubane was devoid of Rydberg excitations.

### 3.2 Octaazapentalene

We note that reduction in symmetry reduces surprisingly the transition energy. This is obvious because the lowest transition in octaazapentalene predicted at 3.369 eV lies about 3eV below the lowest transition in octaazacubane. This transition is  $n \rightarrow \pi^*$  transition with an oscillator strength of 0.0450. Comparing the spectra of the three isomers we notice that the lowest transition in octaazacubane is  $n \rightarrow \sigma^*$  while this is  $n \rightarrow \pi^*$  in Octaazapentalene and octaazacuneane. Among  $n \rightarrow \pi^*$  transitions the most absorbing one is predicted at 5.179 eV with an oscillator strength of 0.0816. This  $n \rightarrow \pi^*$  transition is x-polarized. The most intense of all the transitions

in octaazapentalene is an  $n \rightarrow \sigma^*$  transition at 7.76 eV. This maximum absorbing band having oscillator strength of 0.5699 is x-polarized. Thus the maximum absorption region in octaazapentalene occurs around 8 eV.

The spectrum of Octaazapentalene consists of two Rydberg excitations, the former at 5.416 eV has a quantum defect of 1.3 while the latter at 6.823 eV has a quantum defect of 1.1. Thus they form the members of ns Rydberg series. These Rydberg excitations exhibit zero oscillator strength. We would like to mention here that both of the Rydberg members are overlapped by intense transitions on both of their ends. So it would be difficult to observe them experimentally.

### 3.3 Octaazacuneane

The lowest excitation in octaazacuneane is an  $n \rightarrow \pi^*$  at 4.921eV. This transition shows oscillator strength of 0.0012. We would like to mention here the polarization of the lowest excitation in the  $N_8$  isomers. This is z-polarized in octaazacubane and octaazapentalene while in octaazacuneane this is y-polarized, The lowest symmetry of octaazacuneane (as compared with the symmetry of octaazacubane or octaazapentalene) makes  $n \rightarrow \pi^*$  transitions more dominant than  $n \rightarrow \sigma^*$  transitions. This is because the most intense of all the transitions in octaazacuneane is an  $n \rightarrow \pi^*$  at 7.883 eV. This transition having an oscillator strength of 0.1942 is y-polarized. Thus the maximum absorption in octaazacuneane occurs around 8eV ; this is the same absorption region as mentioned in octaazacubane and octaazapentalene. Tian et al. [8] opine that for the  $N_8$  isomers with the same bonding characteristics, it appears that the ones with higher symmetry have the higher energy. Here if we consider the lowest excitation energy then their ordering is

$$O_h N_8 < C_{2v} N_8 < D_{2h} N_8$$

Comparing the spectra of the isomers we note that the spectrum of octaazapentalene or octaazacuneane is more structured than that of octaazacubane.

The spectrum of octaazacuneane comprises three Rydberg excitations. The first at 7.145 eV exhibits intensity ( $f= 0.004$ ) and its quantum defect of 1.13 does indicate that this forms the member of ns Rydberg series. This transition on account of its intensity can be observed experimentally. The other two transitions at 7.409 and 7.425 eV again form the members of ns Rydberg series because their respective quantum defects are 1.06 and 1.05. These transitions are forbidden and hence they can produce difficulties in their experimental observation.

### IV. Triplet excitations

The lowest triplet excitation in octaazacubane is an  $n \rightarrow \sigma^*$  transition while in octaazapentalene and octaazacuneane this is an  $n \rightarrow \pi^*$  one. All the singlet — triplet splittings in octaazacubane do not exceed 1eV. In octaazapentalene and octaazacuneane some of the S — T splittings exceed 1 eV. An important point is that only the S-T splittings of  $n \rightarrow \pi^*$  transitions in octaazapentalene and octaazacuneane exceed 1 eV while those of  $n \rightarrow \sigma^*$  transitions remain less than 1 eV, The  $n \rightarrow \pi^*$  transitions in all the three isomers exhibit intensity. The separations between the lowest singlet and triplet  $n-\pi$  states are as follows. This is about 0.612 eV in octaazacubane, 1.124 eV in octaazapentalene and 0.534 eV in octaazacuneane.

### V. Conclusion

The electronic spectra of octaazacubane, octaazapentalene and octaazacuneane have not yet been observed or theoretically calculated, except Ref. [10], in the literature. Our calculations reveal that the spectra of the  $N_8$  isomers are compact. Nevertheless, the structural features of the spectra are well pronounced. We note the ordering of different spectroscopic data of the isomers as follows.

The first ionization potential:

$$D_{2h} N_8 < O_h N_8 < C_{2v} N_8$$

The maximum absorption region:

$$O_h N_8 < D_{2h} N_8 < C_{2v} N_8$$

The lowest S-T splitting

$$C_{2v} N_8 < O_h N_8 < D_{2h} N_8$$

We hope that the present results would be helpful in further studies.

**Table 1.** The singlet excitations in  $N_8$  isomers (All the energies are in eV)

Molecule (Symmetry)	Previous Work			This Work					% Rydberg cha.
	Transition n Energy	f	Type of transition	Transition n energy	F	Pol.	Sym. Of exc. state	Type of transition	N
Octaaz-Acubana ( $O_h$ )	5.842	0	$T_{2u}(n \rightarrow \sigma^*)$	6.296	0.0374	z	$T_{1u}$	$n \rightarrow \sigma^*$	0

	5.847	0	$A_{1g}(n \rightarrow \sigma^*)$	6.312	0.000	-	$A_{2g}$	$n \rightarrow \sigma^*$	0
	5.850	0	$A_{1g}(n \rightarrow \pi^*)$	6.316	0.000	-	$T_{2g}$	$n \rightarrow \pi^*$	0
	5.857	0	$A_{2g}(n \rightarrow \sigma^*)$	6.321	0.0439	y	$T_{2g}$	$n \rightarrow \pi^*$	0
	5.867	0	$T_{2g}(n \rightarrow \pi^*)$	6.332	0.000	-	$A_{2g}$	$n \rightarrow \pi^*$	0
Octaazapentalene( $D_{2h}$ )				3.369	0.0450	z	$B_{1u}$	$n \rightarrow \pi^*$	0
				3.505	0.0000	-	$B_{2u}$	$n \rightarrow \pi^*$	0
				3.511	0.0000	-	$A_u$	$n \rightarrow \pi^*$	0
				3.778	0.0000	-	$B_{3u}$	$n \rightarrow \sigma^*$	0
				3.824	0.0000	-	$B_{3u}$	$n \rightarrow \sigma^*$	0
Octaazacuneane ( $C_{2v}$ )				4.921	0.0012	y	$A_1$	$n \rightarrow \pi^*$	0
				4.988	0.0050	x	$B_1$	$n \rightarrow \pi^*$	0
				5.175	0.0115	z	$A_2$	$n \rightarrow \pi^*$	0
				5.346	0.0000	-	$A_1$	$n \rightarrow \sigma^*$	0
				5.528	0.0094	x	$B_1$	$n \rightarrow \sigma^*$	0

**Table 2.** The Triplet excitations in  $N_8$  isomers (All the energies are in eV\*)

Molecule (Symmetry)	Previous Work			This Work				% Rydberg cha.
	Transition energy	S-T split	Type of transition	Transitio n energy	S-T split	Sym. Of exc. State	Type of transition	N
Octaaz- Acubana ( $O_h$ )	5.375	0.609	$T_{2g}(n \rightarrow \pi^*)$	5.708	0.580	$T_{1u}$	$n \rightarrow \sigma^*$	0
	5.377	0.736	$T_{1g}(n \rightarrow \pi^*)$	5.709	0.612	$T_{2g}$	$n \rightarrow \pi^*$	0
	5.510	0.332	$T_{2u}(n \rightarrow \sigma^*)$	5.713	0.643	$A_{1g}$	$n \rightarrow \sigma^*$	0
	5.546	0.556	$T_{1g}(n \rightarrow \pi^*)$	5.983	0.355	$T_{1u}$	$n \rightarrow \sigma^*$	0
	5.555	0.302	$A_{2g}(n \rightarrow \sigma^*)$	6.031	0.285	$T_{2g}$	$n \rightarrow \pi^*$	0
Octa Azapentalene ( $D_{2h}$ )				2.245	1.124	$B_{1u}$	$n \rightarrow \pi^*$	0
				2.662	1.106	$B_{3u}$	$n \rightarrow \pi^*$	0
				2.688	2.309	$B_{2g}$	$n \rightarrow \pi^*$	0
				2.761	0.744	$B_{2u}$	$n \rightarrow \pi^*$	0
				3.213	0.655	$B_{3u}$	$n \rightarrow \pi^*$	0
Octaazacuneane ( $C_{2v}$ )				4.464	0.534	$A_1$	$n \rightarrow \pi^*$	
				4.608	0.567	$A_2$	$n \rightarrow \pi^*$	0

				4.643	0.703	A <sub>1</sub>	n→σ*	0
				4.717	0.204	A <sub>1</sub>	n→π*	0
				4.849	0.949	B <sub>2</sub>	n→π*	2

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