

MRINDO/S calculation on the electronic spectra of N₂H₂ isomers

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Abstract MRINDO/S calculations augmented by singly excited configuration interaction were performed on the isomers of N₂H₂. Electronic configurations, ionization potentials and electronic spectra of the isomers are presented. The importance of outer (Rydberg) orbitals is stressed and it is found that a number of singlet-singlet transitions of the isomers lead to excited states with considerable Rydberg characters.

Keywords N₂H₂ isomers, ionization potentials, electronic spectra

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1. Introduction

Diazine (N₂H₂) has been the subject of numerous experimental and theoretical investigations [1–5]. Its ground state is the planar singlet species which has a trans structure of C_{2h} symmetry. Trans-diazine is well characterized experimentally. Two other low-lying stable singlet species have been identified by theoretical studies; these are also planar and both have C_{2v} symmetry. One is cis-diazine, while the second is iso-diazine (or amino nitrene). A very limited amount of experimental information is available for cis- and iso-diazine derived from gas phase and/or matrix isolation studies. Whitelegg and Woolley [5] have reported ionization potentials and vibrational frequencies spectra of these isomers. But there is scarcity of literature regarding their electronic spectra. This led us to consider these species. Here, we report the calculated electronic spectra of the isomers of diazine : trans-diazine, cis-diazine and iso-diazine. The optimized geometrical parameters, bond lengths in Angstrom and bond angles in degree, of the isomers were taken from Whitelegg and Woolley [5].

2. Outline of the work

In the present method, MRINDO/S, we added H2s, H2p, N3s and N3p Slater atomic orbitals to the basis. The details of the methodology have been given by Prasad and Rai [6].

In the present calculation, the energy of the ground state was first minimized in the usual way. The configuration interaction was applied including the lowest thirty singly excited configurations for both the singlets and triplets. Jacobi diagonalization iterations were continued until all off-diagonal elements were smaller than 10⁻⁴ a.u. and the SCF (self-consistent field) procedure was terminated when all eigenvalues agreed within 10⁻³ a.u. between two successive iterations.

3. Results

Table 1 contains the Koopmans [7] theorem ionization potentials and the corresponding orbital symmetries. The *ab initio* value for IP'S (ionization potentials) and symmetry of orbitals are given in the first columns. These were taken from Whitelegg and Woolley [5].

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Table 1. The lowest ionization potentials of N₂H₂ isomers (eV)

Molecule (symmetry)	<i>ab initio</i> ^a		MRINDO/S		
	IP	Sym of orbital	IP	Sym. of orbital	Type
Trans-diazine (C _{2h})	10.80	a _g	1.05	a _g	σ
			12.81	a _u	π,n
			15.91	b _u	σ
			16.13	a _g	σ
			25.26	b _u	σ
			37.09	a _g	σ
Cis-diazine (C _{2v})	10.88	b ₂	11.73	b ₂	σ
			12.82	b ₁	π,n
			13.14	a ₁	σ,n
			19.25	a ₁	σ
			24.04	b ₂	σ
			37.04	a ₁	σ
Iso-diazine (C _{2v})	9.58	b ₂	10.45	b ₂	σ,n
			12.84	b ₁	π,n
			14.77	a ₁	σ,n
			18.65	b ₂	σ
			24.78	a ₁	σ
			36.75	a ₁	σ

^aRef [5]

Table 2 contains the lower singlet-singlet excitation energies, oscillator strengths, and symmetries of the excited states as computed in the approximation used by Prasad and Rai [6]. The last columns of Table 2 contain the percentage Rydberg characters of the states. The first columns of Table 2 contain experimental transition energies [8,9]. Table 3 gives transition energies, symmetries of the excited states, and splittings of the five lowest singlet-triplet transitions of each species.

The results are compared mostly with the *ab initio* values cited in Tables 1 and 2; otherwise proper references are noted.

4. Discussion

4.1. Charge distribution and cis-trans barrier :

The net charge distribution in diazine isomers is shown in Figure 1. According to general chemical intuition, the higher the positive charge on H in a compound, the higher is its acidic character. So, more easily it may be replaced by metal. The higher the electron density on N, the higher is its donor character and hence the higher is its basic character. Due to increase in negative charge density on N, its size is slightly increased. If positive charge is developed on N, its donor

Table 2. Lower Singlet-Singlet transitions in N₂H₂ isomers All energies are in eV

Molecule (Symmetry)	Experimental ^{a,b}		MRINDO/S				% Rydberg character		
	Transition energy	Type of transition	Transition energy	<i>f</i>	Sym of excited state	Type of transition	H	N	Total
Trans-diazine (C _{2h})	3.54	n→π*	1.97	0.000	B _g	σ→π*	0	0	0
	6.32	n→3s	5.67	0.081	B _u	n→π*	3	5	8
	8.68	n→3p	6.90	0.000	B _g	σ→π*	0	0	0
			7.23	0.000	A _u	σ→π*	0	0	0
			7.67	0.132	B _u	σ→σ*	3	6	9
			7.83	0.000	A _g	σ→σ _R *	36	54	90
			8.17	0.000	B _g	n→σ*	5	12	17
			8.18	0.000	A _g	σ→σ _R *	43	52	95
			8.64	0.005	B _u	σ→σ _R *	30	60	90
		8.76	0.002	B _u	σ→σ _R *	39	58	97	
Cis-diazine (C _{2h})			2.92	0.000	B ₁	σ→π*	0	0	0
			3.83	0.000	A ₂	n→π*	0	0	0
			5.78	0.101	B ₂	n→π*	1	1	2
			7.41	0.041	A ₁	σ→σ*	4	4	8
			7.88	0.000	A ₂	n→σ*	3	4	7
			8.38	0.042	B ₂	σ→σ _R *	32	39	71
			8.87	0.001	B ₂	σ→σ _R *	30	59	89
			9.15	0.000	B ₁	n→σ _R *	30	42	72
			9.19	0.000	A ₁	σ→σ _R *	23	72	95
		9.49	0.000	A ₁	σ→σ _R *	31	63	94	

Table 2. (Cont'd.).

Molecule (Symmetry)	Experimental ^{a,b}		MRINDO/S				% Rydberg character		
	Transition energy	Type of transition	Transition energy	f	Syn. of excited state	Type of transition	H	N	Total
Iso-diazine (C_{2v})			1.24	0.000	A_2	$n \rightarrow \pi^*$	0	0	0
			4.34	0.005	B_2	$n \rightarrow \pi^*$	1	1	2
			6.25	0.075	A_1	$n \rightarrow \pi^*$	0	0	0
			6.59	0.000	B_1	$n \rightarrow \pi^*$	0	0	0
			6.99	0.000	B_1	$n \rightarrow \sigma^*$	0	1	1
			7.35	0.000	B_2	$n \rightarrow \sigma_R^*$	26	74	100
			7.96	0.000	B_2	$n \rightarrow \sigma_R^*$	28	71	99
			8.09	0.000	A_1	$n \rightarrow \sigma_R^*$	22	78	100
			8.13	0.000	A_2	$n \rightarrow \pi_R^*$	18	82	100
		8.40	0.000	B_2	$n \rightarrow \sigma_R^*$	31	68	99	

^aRef. [8], ^bRef. [9]

character is diminished and hence its basic character is decreased. On this ground, the H atoms in iso-diazine seem to be more acidic than in trans- and cis-diazine. The nitrogen atom in iso-diazine, attached to hydrogen atoms, loses its donor character, while the other nitrogen atom gets much more donor character. In trans- and cis-diazine, the bonding pair of electrons between N and H gets shifted towards N making it slightly negatively charged.

Table 3. The five lowest singlet-triplet transitions in N_2H_2 isomers. All energies are in eV.

Molecule (Symmetry)	MRINDO/S				% Rydberg character		
	Transition energy	S-T split	Sym. of excited state	Type of transition	H	N	Total
Trans-diazine (C_{2h})	0.95	1.02	B_g	$\sigma \rightarrow \pi^*$	0	0	0
	1.80	3.87	B_u	$n \rightarrow \pi^*$	0	0	0
	5.76	1.47	A_u	$\sigma \rightarrow \pi^*$	0	0	0
	5.86	1.81	B_u	$\sigma \rightarrow \sigma^*$	7	13	20
	6.37	0.53	B_g	$\sigma \rightarrow \pi^*$	0	0	0
Cis-diazine (C_{2v})	1.78	4.00	B_2	$n \rightarrow \pi^*$	0	0	0
	1.89	1.03	B_1	$\sigma \rightarrow \pi^*$	0	0	0
	2.79	1.04	A_2	$n \rightarrow \pi^*$	0	0	0
	6.43	0.98	A_1	$\sigma \rightarrow \sigma^*$	0	4	4
6.98	1.40	A_2	$n \rightarrow \sigma^*$	0	4	4	
Iso-diazine (C_{2v})	0.25	0.99	A_2	$n \rightarrow \pi^*$	0	0	0
	3.06	3.19	A_1	$n \rightarrow \pi^*$	0	0	0
	3.65	0.69	B_2	$n \rightarrow \sigma^*$	1	1	2
	4.83	1.76	B_1	$n \rightarrow \pi^*$	0	0	0
	5.29	1.70	B_2	$n \rightarrow \sigma^*$	0	1	1

The computed cis-trans barrier is about 2.21 eV, while the barrier height calculated at the SCF level of *ab initio*

theory [5] is about 0.11 hartree (~2.97 eV). Thus our calculation agrees reasonably with the *ab initio* one.

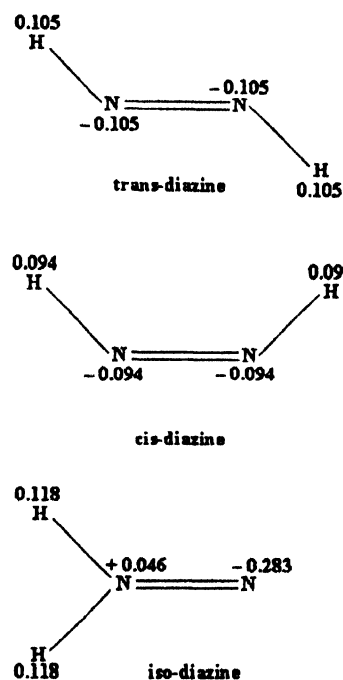


Figure 1. The net charge distribution in diazines.

4.2. Quantum defect :

The energies of Rydberg states, formed by excitation of a single electron to a Rydberg orbital can be represented in a good approximation by a Rydberg formula [10]

$$E_n = A - \frac{R}{(n - \delta)^2},$$

where A is the ionization potential toward which the series converges as n runs serially to infinity, R is the Rydberg constant, and δ is called the quantum defect. For molecules

built-up from atoms of the first period, δ is small (≤ 0.1) for states derived from nd electrons, somewhat larger (0.3–0.5) for np electrons and appreciably large (0.9–1.2) for ns electrons.

4.3. Ionization potentials :

The *ab initio* calculations predicted the following configurations for the stable singlet species :

trans-diazine	:	a_g	b_u	b_u	a_g	a_u	a_g
cis-diazine	:	a_1	b_2	a_1	a_1	b_1	b_2
iso-diazine	:	a_1	a_1	b_2	b_1	a_1	b_2

Each of these orbitals is filled with two electrons. The present calculation predicts these configurations as follows.

trans-diazine	:	a_g	b_u	a_g	b_u	a_u	a_g
cis-diazine	:	a_1	b_2	a_1	a_1	b_1	b_2
iso-diazine	:	a_1	a_1	b_2	a_1	b_1	b_2

It is evident therefore that the present configurations are consistent with that of *ab initio* calculations except single reversal of states in trans- and iso-diazine. According to these configurations we infer that these species contain only one occupied π MO associated with the orbital symmetries : a_u in trans-diazine and b_1 in cis- and iso-diazine.

The lowest occupied MO of these isomers is assigned an in-plane σ orbital. This is consistent with the *ab initio* calculation. In addition, the calculated first ionization potentials of the isomers are comparable with the *ab initio* prediction. The important aspect of the present calculation is that the second ionization potential of the isomers corresponds to the removal of an electron from a lone pair π orbital. This ensures that the $n \rightarrow \pi^*$ transitions occurring in the spectra of these isomers must exhibit intensity. Such a situation is not found in higher azines : pentazine and isomers of *s*-triazine and *s*-tetrazine [6,11]. This aspect of the spectra will be discussed in succeeding section. We note that the first IP of the isomers follows the trend

$$\text{iso-diazine} < \text{trans-diazine} < \text{cis-diazine}.$$

This is again in accord with the *ab initio* calculation.

4.4. Singlet excitations :

(i) Trans-diazine

The $n \rightarrow \pi^*$ transitions cause weak bands in the visible or the near or the medium ultraviolet; the overall energy region ranges from about 1.7 to 6.2 eV. We note only one $n \rightarrow \pi^*$ transition in trans-diazine at 5.67 eV. The overall symmetry of the state is B_u and hence it is electric dipole allowed with x and y components of dipole moment vector. It has an oscillator strength of 0.081. The computed transition energy to $n \rightarrow \pi^*$ seems higher than experimental one [8].

The $n \rightarrow \pi^*$ transition in pyridazine, pyrimidine and pyrazine is observed [12] at 3.30, 3.85 and 3.82 eV with respective oscillator strength of 0.0058, 0.0069 and 0.01. The calculated [13] sequence of energy is 3.12, 4.01 and 3.53 eV whereas the sequence of oscillator strength is 0.016, 0.015 and 0.014. In higher azines, *s*-triazine and *s*-tetrazine, weakly allowed $n\pi^*$ states have been predicted [6] while in pentazine and the isomers of *s*-triazine and *s*-tetrazine none of the $n \rightarrow \pi^*$ transitions exhibited intensity [6,11]. In this context the $n \rightarrow \pi^*$ transition in trans-diazine seems to be more intense. The spectrum of trans-diazine does not comprise $\pi \rightarrow \pi^*$ transition, for its configuration contains only one originating (occupied) π MO which is assigned a lone pair MO. Trombetti [8] argued on his experimental observation that $\pi \rightarrow \pi^*$ in trans-diazine is lost somewhere in the maze of absorption beyond 7000 cm^{-1} ($\sim 8.68 \text{ eV}$). The maximum absorption in trans-diazine occurs at about 7.67 eV. The band associated with the maximum absorption is $\sigma \rightarrow \sigma^*$ which has an oscillator strength of 0.132.

Series of Rydberg states in trans-diazine arise not only by taking an electron from the most loosely bound orbital (non-bonding orbital) but also by taking it from bonding orbital occupied in the ground state. Out of thirty SCF states, excluding valence states, most arise by taking an electron from bonding orbital and few of them are weakly allowed by symmetry. Rydberg states which arise due to the removal of an electron from non-bonding orbital are all symmetry forbidden. The overall symmetry state of allowed Rydberg bands is B_u .

Rydberg excitations in trans-diazine set in at 7.83 eV; this in pyrimidine and pyrazine sets in at 6.97 and 6.83 eV respectively. Rydberg excitations in pyridazine have not been observed [12]. The first two members of Rydberg band in trans-diazine at 7.83 and 8.18 eV possess respective quantum defects (δ) of 0.95 and 0.83 and hence correspond to the members of *ns* Rydberg series. Thus the first *ns* Rydberg band is in a reasonable agreement with experiment [9]. The next band at 8.64 eV with $\delta = 0.63$ forms the member of *np* Rydberg series and agrees well with experimental one [9]. This is then followed by a number of closely spaced Rydberg bands and hence we discuss the spectrum no further.

(ii) Cis-diazine

We note a forbidden ($f = 0.00$) $n \rightarrow \pi^*$ transition at 3.83 eV and thus this energy value agrees well with experimental one for trans-diazine. The forbiddance arises due to the fact that the overall symmetry of the $n\pi^*$ state is $A_1 \times A_2 = A_2$ and none of the components of dipole moment vector M has symmetry A_2 ; consequently the matrix element of the transition moment vanishes. In general, $A_2 - A_1$ transitions

of C_{2v} are rigorously forbidden for electric dipole radiation can occur as magnetic dipole radiation. On the other hand, we note another $n\pi^*$ state of state symmetry B_2 at 5.78 eV which is allowed with the y component of the dipole moment vector. It has an oscillator strength of 0.101. Similar to trans-diazine, the spectrum of cis-diazine does not reveal $\pi \rightarrow \pi^*$ transitions. The maximum absorption in cis-diazine occurs at about 9.88 eV. The band associated with the maximum absorption is $n \rightarrow \sigma^*$ which has an oscillator strength of 0.248.

As to the Rydberg excitations, the first two bands at 8.38 and 8.87 eV have respective quantum defects of 0.99 and 0.83 and thus from the members of ns Rydberg series. The members at 9.15 and 9.19 eV with respective δ values of 0.71 and 0.69 belong to np Rydberg series. Thus we note some enhanced values for ns and np Rydberg bands as compared to the bands in trans-diazine. This is then followed by a number of Rydberg excitations. In cis-diazine Rydberg bands with state symmetry B_2 seem to be allowed and the one at 8.38 eV is the most intense which has an oscillator strength of 0.042. This lies about 1.5 eV below the maximum absorption band.

(iii) Iso-diazine

The number of occupied lone pair orbital increases as we move from trans-diazine to iso-diazine : one in trans-, two in cis-, and three in iso-diazine. Consequently, to all of the excitations in iso-diazine the originating orbital is a lone pair orbital. We note the lowest singlet A_2 ($n \rightarrow \pi^*$) state at 1.24 eV which is forbidden by symmetry. The next $n \rightarrow \pi^*$ transition at 6.25 eV is intense ($f = 0.075$). The overall symmetry of the state is A_1 and hence this is allowed with z component of dipole moment vector. Thus, the allowed $n \rightarrow \pi^*$ transition in the isomers is predicted at higher energy than experiment. The third $n\pi^*$ state with state symmetry B_1 is predicted to be forbidden ($f = 0.00$) which violates the general selection rule. The B_1 electronic state of C_{2v} is allowed with x component of dipole moment vector. The reason of forbiddenness might be due to the neglect of vibronic interactions, for the general selection rule is valid when vibronic interactions are not neglected. None of the transitions is assigned $\pi \rightarrow \pi^*$. The maximum absorption in iso-diazine occurs at about 10.32 eV; the band associated is $n \rightarrow \sigma^*$ with an oscillator strength of 0.328. Thus, it seems obvious that the $n \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ transitions are the cornerstone of the spectra of N_2H_2 isomers.

Contrary to trans-diazine and cis-diazine, we note only one member of ns Rydberg series at 7.35 eV with $\delta = 0.92$. The first member of np Rydberg series appears at 7.96 eV with $\delta = 0.66$. This is then followed by a number of closely spaced Rydberg bands. The Rydberg bands are very weak

as compared to the bands in trans- and cis-diazine. We note that the ns and np Rydberg bands in iso-diazine are in a reasonable agreement with experimental ones for trans-diazine.

4.5. Triplet excitations :

The experimental benchmarks of the calculations are the separations between the lowest singlet $\pi-\pi$ and $n-\pi$ states, the separations between the lowest singlet and triplet $n-\pi$ states, and the intensities of allowed $n-\pi^*$ transitions. As discussed in the preceding sections, the spectra of the isomers are devoid of $\pi-\pi$ states and hence question of separations of the lowest singlet $\pi-\pi$ and $n-\pi$ states does not arise. The intensities of allowed $n-\pi^*$ transitions have already been discussed. To the remaining part, we predict the separations between the lowest singlet and triplet $n-\pi$ states as follows. This is about 3.87 eV in trans-diazine, 4.00 eV in cis-diazine, and 0.99 eV in iso-diazine. The low value of the separation in iso-diazine may be attributed to its structure in which the two hydrogen atoms are attached to a single nitrogen atom. However, this separation in iso-diazine is comparable to the corresponding separations in higher azines [6, 11]. Triplet Rydberg bands are also predicted whose $S-T$ splits are too small.

5. Conclusion

The presence of nitrogen atoms causes the appearance of lone pair level which is characterized by very high coefficients of $2S_N$ and $2P_N$ in the molecular orbital. These orbitals clearly cannot be termed non-bonding since the first ionization potential of any isomers is > 10 eV. The total populations in the isomers based upon a Mulliken population analysis show that the nitrogen atoms are over all sp^2 hybridized. The $n \rightarrow \pi^*$ transitions in the isomers exhibit intensity. In going from trans- to iso-diazine, the maxima in the absorption bands show hyperchromic effect. These bands, on account of their high intensity, can be easily observed. On the other hand, Rydberg bands in the isomers are less intense which may be observed under appropriate experimental conditions.

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