

MRINDO/S-CI calculation on the electronic spectra of higher azines

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Summary. MRINDO/S calculation completed by singly excited configuration interaction was performed on the higher azines *s*-triazine, *s*-tetrazine and pentazine. The results enable the main characteristics of the observed electronic spectra to be interpreted. 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.

Key words: Spectroscopic MRINDO/S – *s*-Triazine – *s*-Tetrazine – Pentazine

1. Introduction

The semi-empirical scheme developed by Pople [1] by incorporating Pariser and Parr's assumptions [2] into the Roothaan's LCAO-MO theory is popularly known as the PPP method. This method was originally formulated within the π -electron approximation. This and some of the other approximations of this method are also used in other schemes such as CNDO (complete neglect of differential overlap) and INDO (intermediate neglect of differential overlap) [3, 4]. The significant difference between PPP and these methods (CNDO, INDO) is that CNDO and INDO treat all valence electrons explicitly whereas PPP explicitly treats only the electrons in π orbitals.

Del Bene and Jaffe, using the configuration interaction (CI) technique, have discussed the applicability of the CNDO method to the spectroscopy of molecules containing π and lone-pair (n) electrons [5, 6]. They evaluated Coulomb integrals semi-empirically, introduced K , a parameter to differentiate the resonance integrals $\beta_{\pi,\pi}$ from $\beta_{\sigma,\sigma}$, and readjusted β_{AB}° the so-called bonding parameters. With these modifications the CNDO-CI method turns out as a useful tool for the interpretation of the electronic spectra of rather large molecules containing π and n (non-bonding) electrons. Nevertheless, INDO is preferred over CNDO as the former includes the one-centre exchange integrals necessary for accurately separating different terms from within a configuration. The effect of neglecting such integrals is that the singlet and triplet arising from $n \rightarrow \pi^*$ transitions are degenerate within the CNDO approximation. Krogh-Jespersen and Ratner, following the idea of Del Bene and Jaffe, used the INDO

model to account for the photoelectron spectrum of benzonitrile and found encouraging results [7].

All of these methods used a minimum basis set of valence-shell AO (atomic orbitals), and thus could not account for transitions which involve a change in principal quantum number. The use of extended basis sets in semi-empirical methods has received little attention. Salahub and Sandorfy [8] proposed an RCNDO method, where R stands for Rydberg and excited atomic orbitals, in which higher (Rydberg) atomic orbitals were included in the basis of ordinary CNDO. The RCNDO method excludes one-centre exchange integrals, and thus could not account for singlet-triplet splitting of an $n \rightarrow \pi^*$ type transition (this is exactly what we expected within the CNDO approximation). To overcome this deficiency of the RCNDO method a similar basis set was used in INDO, and the method thus developed was termed RINDO (Rydberg INDO) [9].

In the RCNDO and RINDO methods the overlap integrals are treated on an equal footing, and thus these methods cannot account for the effect of the σ electrons on the energy levels of π electrons. With the aim of gaining information on this effect, we adapted the RINDO method and proposed a method, which we called, following Del Bene and Jaffe, RINDO/S (S for screening or spectral) [10]. The method we employ in the present work is a modification of RINDO/S. This method ignores insignificant interactions involving Rydberg atomic orbitals that are required in the RINDO/S method. Thus this method, which is intermediate in complexity between RCNDO and RINDO/S, was termed MRINDO/S (modified RINDO/S). We have applied this method with some success to prediction of transition energies, oscillator strengths, Rydberg characters and ground-state properties for small organic molecules [11]. We report here the application of this method to elucidation of the electronic spectra of *s*-triazine, *s*-tetrazine and pentazine. This represents a rather stringent test of the method, since they contain π and lone-pair electrons and exhibit $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. These molecules are of great interest to spectroscopists and theoretical chemists.

2. Outline of the work

In the MRINDO/S method we added to the basis H $2s$, H $2p$, C $3s$, C $3p$, N $3s$, and N $3p$ Slater atomic orbitals. The approximation described below ensures that the method is invariant to the choice of internal axes.

Besides the neglect of differential overlap we make the following approximations: The electron repulsion integrals $r_{\mu\lambda}$ depend only on the atoms, say A and B, to which the orbitals μ and λ belong and on their principal quantum numbers, say n_1 and n_2 , respectively. Thus,

$$r_{\mu\lambda} = r_{n_1(A)n_2(B)}. \quad (1)$$

The core integrals are treated in the RCNDO manner [8], i.e.,

$$\begin{aligned} H_{\mu\nu} &= (\mu | (-\frac{1}{2})\nabla^2 - V_A | \nu) - \sum_{B \neq A} (\mu | V_B | \nu) \\ &= U_{\mu\mu} - \sum_{B \neq A} (\mu | V_B | \mu) \quad \mu \text{ on } A, \end{aligned} \quad (2)$$

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B \neq A} (\mu | V_B | \nu) \quad \mu, \nu \text{ on the same centre} \quad (3)$$

$$= \beta_{\mu\nu} \quad \mu, \nu \text{ on different centres.} \quad (4)$$

The terms $(\mu | V_B | \mu)$ for all orbitals on the same atom with the same principal quantum number are taken to be equal. We set

$$(\mu | V_B | \mu) = V_{n_1(AB)},$$

where $V_{n_1(AB)}$ represents the interaction of an orbital μ on atom A (and belonging to the principal quantum number n_1) with the core of atom B. If we approximate this core by a valence-shell one-electron distribution multiplied by the nuclear charge, we have [8]

$$V_{n_1(AB)} = Z_B r_{n_1(A)n_v(B)}, \quad (5)$$

where $n_{v(B)}$ is the principal quantum number of the valence-shell of atom B.

If we use pure atomic orbitals

$$U_{\mu\nu} = 0$$

since μ and ν are on the same centre [12]. We neglect the remaining terms of (2). This is consistent with the neglect of differential overlap.

$\beta_{\mu\nu}$ is taken to be proportional to the overlap integrals with the factor of proportionality depending only on the atoms to which μ and ν belong. This is necessary for invariance. Thus,

$$\beta_{\mu\nu} = \beta_{n_1(A)n_2(B)}^\circ S_{\mu\nu} \quad (6)$$

and the elements of the Hartree-Fock (HF) matrix under the RINDO/S scheme become [10]:

$$\begin{aligned} F_{\mu\mu} = & U_{\mu\mu} + \sum_{\lambda}^{A, n_1} p_{\lambda\lambda} [(\mu\mu | \lambda\lambda) - \frac{1}{2}(\mu\lambda | \mu\lambda)] \\ & + \sum_{n_2 \neq n_1}^A P_{n_2(A)n_2(A)} \Gamma_{n_1(A)n_2(A)} \\ & + \sum_{B \neq A} \left(\sum_{n_2}^B P_{n_2(B)n_2(B)} \Gamma_{n_1(A)n_2(B)} - Z_B \Gamma_{n_1(A)n_v(B)} \right), \quad \mu \rightarrow n_1(A), \end{aligned} \quad (7)$$

$$F_{\mu\nu} = p_{\mu\nu} \left[\frac{3}{2}(\mu\nu | \mu\nu) - \frac{1}{2}(\mu\mu | \nu\nu) \right], \quad \mu \neq \nu \rightarrow n_1(A), \quad (8)$$

$$F_{\mu\nu} = \beta_{n_1(A)n_2(B)}^\circ S_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \Gamma_{n_1(A)n_2(B)}, \quad \mu \rightarrow n_1(A); \nu \rightarrow n_2(B). \quad (9)$$

Further, with the approximation mentioned in (1), the one-centre exchange integrals transform as

$$(\mu\nu | \lambda\sigma) = \delta_{\mu\nu} \delta_{\lambda\sigma} \Gamma_{n_1(A)n_2(B)}.$$

Such integrals are necessary in order to account for the separation of atomic states arising from the same configuration, the spin density in σ orbitals, and the singlet-triplet splittings for molecular transitions which involve no common AO in the initial or final orbitals. These can be evaluated in terms of Slater-Condon factors [12]. The exchange integrals involving excited AO's may, however, be ignored in the RCNDO manner. They are expected to be small. Thus we make

the following approximation:

$$(\mu\nu | \lambda\sigma) = \delta_{\mu\nu} \delta_{\lambda\sigma} r_{n_1(A)n_2(B)},$$

unless $(\mu\nu | \lambda\sigma)$ are valence-shell one-centre exchange integrals.

Thus the HF matrix elements under MRINDO/S become [11]

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{\lambda}^{A, n_1} p_{\lambda\lambda} [(\mu\mu | \lambda\lambda) - \frac{1}{2}(\mu\lambda | \mu\lambda)] \\ + \sum_{n_2 \neq n_1}^A P_{n_1(A)n_2(A)} r_{n_1(A)n_2(A)} \\ + \sum_{B \neq A} \left(\sum_{n_2}^B P_{n_1(B)n_2(B)} r_{n_1(A)n_2(B)} - Z_B r_{n_1(A)n_b(B)} \right), \quad \mu \rightarrow n_1(A), \quad (10)$$

$$F_{\mu\nu} = \beta_{n_1(A)n_2(B)}^{\circ} S_{\mu\nu} - \frac{1}{2} p_{\mu\nu} r_{n_1(A)n_2(B)}, \quad \mu \rightarrow n_1(A); \nu \rightarrow n_2(B). \quad (11)$$

These are just the RCNDO HF matrix elements.

The significant difference between the RCNDO and the MRINDO/S methods is that the former neglects all one-centre exchange integrals whereas the latter retains the integrals which involve only the valence-shell AO's and, in addition, screens the π -type interactions.

The integrals were evaluated in the following way:

(a) Ionization potentials and electron affinities for valence orbitals were taken from Pople and Segal [3b]. For the outer orbitals, average ionization potentials were taken from Salahub and Sandorfy [8]. Electron affinities for these were neglected as they are expected to be small.

(b) Two-electron integrals were treated as follows:

(i) One-orbital integrals:

$$(\mu\mu | \mu\mu) = r_{n_1(A)n_1(A)} = I_{n_1(A)} - A_{n_1(A)}.$$

The values for p electrons were those used by Del Bene and Jaffe [5].

(ii) Two-centre integrals $r_{n_1(A)n_2(B)}$ were calculated using Pariser and Parr's [2, 13] uniformly charged sphere extrapolation technique.

(iii) One-centre two orbital integrals:

$$r_{n_1(A)n_2(B)} = \frac{1}{2}(r_{n_1(A)n_1(A)} + r_{n_2(A)n_2(A)}).$$

(c) Resonance integrals.

These integrals were calculated using the semi-empirical expression

$$\beta_{n_1(A)n_2(B)}^{\circ} = \eta(I_{n_1(A)} + I_{n_2(B)}),$$

where $I_{n_1(A)}$ is the average of n_1s and n_1p ionization potentials. η , the bonding parameter, was taken as $\eta = 0.45$ for valence-valence interactions and as $\eta' = 0.045$ for all others. This was necessary to keep the Rydberg orbitals from entering too strongly into the ground state. An appropriate choice of bonding parameters is desirable, since different atomic exchange integrals in the MRINDO/S method may even change the RCNDO assignment (e.g. with $\eta = 0.4$; $\eta' = 0.05$ [8]) of even the lowest energy singlet-singlet transition. This dependence of the nature of the singlet-singlet transition on the

exchange integrals may itself depend upon the particular choice of bonding parameters.

(d) Overlap integrals were calculated with the formulas of Mulliken, Rieke, Orloff and Orloff [14], with π -type interactions screened. Del Bene and Jaffe [5], following an earlier suggestion of Mulliken [15], pointed out that in the Pople-Segal [3b] approximation it might be expected that the effective π - π overlap would be screened differently from the σ - σ overlap. Accordingly, they chose to replace $S_{\mu\nu}$ by

$$\begin{aligned} S_{\mu\nu} &= S_{\mu\nu} && \text{for } \sigma \text{ symmetry} \\ &= kS_{\mu\nu} && \text{for } \pi \text{ symmetry} \end{aligned}$$

The k parameter, for which Del Bene and Jaffe chose the value $k = 0.585$, is the earmark of CNDO/S and MRINDO/S for valence-valence interactions. For other interactions we chose a rational value $k' = 0.595$. The use of such parameters makes the π resonance integral less negative. This less-negative value will tend to raise the energy of the occupied π orbitals, and thus to counteract the tendency for the occupied π MO's (molecular orbitals) to plunge below the σ MO's as is observed when RCNDO or RINDO are used.

In the present calculation the energy of the ground state was first minimized in the usual way. Then configuration interaction was applied including the lowest thirty singly excited configurations for both singlets and triplets. The method was programmed in Fortran IV for the ICL 1900S. 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 successive iterations. CI matrix elements and molecular integrals are given in Appendix A and Appendix B, respectively.

3. Results

Table 1 contains the Koopmans theorem [16] ionization potentials and the corresponding orbital symmetries. The experimental value for IP's (ionization potentials) and symmetry of orbitals are given in the first columns. These were taken from Robin et al. [17] and Fridh et al. [18]. The second columns contain INDO results listed by Ridley and Zerner [19].

Table 2 contains the lower singlet-singlet excitation energies, oscillator strengths and symmetries of the excited states as computed in the approximation described above. Experimental values are given in the first columns. These were taken from Innes et al. [20]. The second columns contain INDO results listed by Ridley and Zerner [19]. The last columns of Table 2 contain the percentage Rydberg characters of the states. Table 3 gives transition energies, symmetries of the excited states, and splittings of the five lowest singlet-triplet transitions of each molecule.

The results are compared mostly with the experimental and INDO values cited in Tables 1 and 2; otherwise proper references are noted. Experimental as well as INDO energy values are cited in eV though they were initially given in cm^{-1} .

Table 1. The seven lowest ionization potentials of azines (in eV)

Molecule (symmetry)	Experimental ^{a,b}			INDO ^c			MRINDO/S		
	I.P.	Symmetry of orbital	Type	I.P.	Symmetry of orbital	Type	I.P.	Symmetry of orbital	Type
C ₃ H ₃ N ₃ (D _{3h})	10.4	e'	σ	10.4	e'		10.38	e'	σ, n
	11.7 ^d	e''	π	11.1	e''	π	11.19	e''	π
	12.2 ^d								
	13.2	a ₁	σ	13.5	a ₁		13.88	a ₁	σ, n
	14.6		π	14.8	e'		14.10	e'	σ
	14.8			15.8	a'' ₁	π	14.90	a'' ₂	π, n
	17.9			21.6	a' ₂		17.01	a' ₂	σ
	22.3			23.6	a' ₁		20.93	a' ₁	σ
	C ₂ H ₂ N ₄ (D _{2h})	9.73	b _{3g}		10.27	b _{3g}		10.27	b _{3g}
11.86		b _{2g}		10.84	b _{2g}		10.84	b _{2g}	π
12.10		a _g		12.00	b _{1u}		11.90	b _{2u}	σ, n
12.85		b _{1g}		12.34	b _{1g}		11.94	b _{1g}	π
15.63		b _{1u}		12.83	a _g		12.08	a _g	σ, n
15.77		b _{3u}		12.96	b _{2u}		12.37	b _{1u}	σ
16.94		b _{1u}		16.24	b _{3u}		15.11	b _{3u}	π
CHN ₅ (C _{2v})							10.24	b ₂	σ, n
							10.99	a ₁	σ, n
							11.47	b ₁	π
							11.72	b ₂	σ, n
							12.05	a ₂	π, n
							13.05	a ₁	σ
						14.97	a ₁	σ	

^a [17]^b [18]^c [19]^d The splitting is attributed to Jahn–Teller effects

4. Discussion

4.1. Ionization potentials

The first few calculated IP's of *s*-triazine are in very good agreement with the experimental values, while the higher calculated values are too low. Robin, Kuebler, and Brundle [17] suggest that the observed values of 11.7 eV and 12.2 eV are associated with e''(π) split by Jahn–Teller effects, and are followed by the e'(10.4 eV) and a'₁(13.2 eV) combinations of the nitrogen lone-pair AO's. This is consistent with our calculation as we find no band between e''(π) and a'₁(σ), and e''(π) is followed by e'(10.38 eV) and a'₁(13.88 eV) combinations of the nitrogen lone-pair AO's. Simple considerations show that the e' – a'₁ splitting in *s*-triazine should be 1.5 times as large as in diazine which is 1.5 eV [21]. The predicted value of 2.25 eV is in adequate agreement with the value of 3.5 eV calculated here for the lone-pair splitting in *s*-triazine. This calculated splitting seems close to the experimental value of 2.8 eV. The INDO value is 3.1 eV for this splitting. The second π ionization in *s*-triazine calculated at 14.9 eV is in very

Table 2. Lowest singlet-singlet transitions in azines. All energies are in eV

Molecule (symmetry)	Experimental ^a		INDO ^b					MRINDO/S					% Rydberg character			
	Energy of max. transitions	<i>f</i>	Symmetry of exc. state	Type of transi- tion	Transi- tion energy	<i>f</i>	Symmetry of exc. state	Type of transi- tion	Transi- tion energy	<i>f</i>	Symmetry of exc. state	Type of transi- tion	H	C	N	Total
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
C ₃ H ₃ N ₃ (D _{3h})	3.9	0.018	A ₂ '	n → π*	4.44	0.00	E''	n → π*	3.20	0.00	E''	n → π*	0	0	0	0
	4.03	Diffuse	E''	n → π*	4.56	0.04	A ₂ '	n → π*	3.20	0.00	E''	n → π*	0	0	0	0
	5.46	0.002	A ₂ '	π → π*	4.77	0.00	A ₁ '	n → π*	3.22	0.02	A ₂ ''	n → π*	0	0	0	0
					5.69	0.00	A ₂ '	π → π*	3.80	0.00	A ₂ ''	n → π*	0	0	0	0
					6.84	0.00	E''	n → π*	5.20	0.00	A ₂ ''	π → π*	0	0	0	0
					7.04	0.00	A ₁ '	π → π*	5.34	0.05	E'	n → σ*	0	0	0	0
					7.60	0.84	E'	π → π*	5.42	0.00	E''	n → π*	0	0	0	0
									6.40	0.00	E'	n → σ*	0	5	0	5
									6.82	0.11	E'	π → π*	0	0	0	0
									6.85	0.12	E'	π → π*	0	0	0	0
								7.06	0.00	A ₂ ''	σ → π*	0	0	0	0	
								7.08	0.02	E'	n → σ*	1	7	1	9	
								7.11	0.03	E'	n → σ*	2	11	4	17	
								7.26	0.00	E''	π → σ*	0	5	0	5	
								7.29	0.002	E'	n → σ _R	11	52	22	85	
								7.87	0.36	E'	π → π*	0	2	0	2	
								7.89	0.36	E'	π → π*	0	0	0	0	

Table 2 (continued)

Molecule (symmetry)	Experimental ^a transitions			INDO ^b					MRINDO/S					% Rydberg character			
	Energy of max.	<i>f</i>	Symmetry of exc. state	Type of transition	Transition energy	<i>f</i>	Symmetry of exc. state	Type of transition	Transition energy	<i>f</i>	Symmetry of exc. state	Type of transition	<i>H</i>	<i>C</i>	<i>N</i>	Total	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
C ₂ H ₂ N ₄ (D _{2h})	2.25	0.0042	B _{3u}	n → π*	2.54	0.023	B _{3u}	n → π*	1.68	0.0035	B _{3u}	n → π*	0	0	0	0	
	3.87	0.001	B _{3u} ?	n → π*	3.96	0.00	B _{1g}	n → π*	3.04	0.00	B _{2g}	n → π*	0	0	0	0	
	4.34		B _{2u}	π → π*	4.28	0.00	A _u	n → π*	3.08	0.00	A _u	n → π*	0	0	0	0	
					4.87	0.19	B _{2u}	π → π*	3.43	0.00	B _{1g}	n → π*	0	0	0	0	
					4.98	0.00	B _{2g}	n → π*	3.46	0.043	B _{2u}	π → π*	0	0	0	0	
									3.54	0.00	A _u	n → π*	0	0	0	0	
									4.73	0.00	B _{1g}	n → π*	0	0	0	0	
									5.26	0.00	B _{3u}	n → π*	0	0	0	0	
									5.43	0.011	B _{2u}	n → σ*	0	0	0	0	
									5.87	0.38	B _{1u}	π → π*	0	0	0	0	
									5.88	0.00	B _{1g}	π → π*	0	0	0	0	
									6.68	0.00	A _g	n → σ*	0	0	0	0	
								7.00	0.00	A _u	n → π*	0	0	0	0		
								7.03	0.00	B _{3g}	n → σ*	1	4	4	9		
								7.15	0.00	B _{3g}	n → σ*	9	40	43	92		
								7.18	0.00	B _{2g}	n → π*	0	0	0	0		
								7.28	0.00	A _u	n → σ*	0	0	0	0		
								7.68	0.00	B _{2g}	n → σ*	9	43	47	99		
								7.69	0.78	B _{1u}	π → π*	0	0	0	0		
								7.79	0.00	B _{1g}	n → σ*	0	0	0	0		
								7.91	0.73	B _{2u}	π → π*	0	0	0	0		

CHN ₅ (C _{2h})	1.87	0.00	B ₁	n → π*	0	0	0	0
	2.42	0.00	A ₂	n → π*	0	0	0	0
	3.05	0.00	B ₁	n → π*	0	0	0	0
	3.47	0.00	A ₂	n → π*	0	0	0	0
	3.77	0.012	B ₂	π → π*	0	0	0	0
	4.69	0.00	A ₂	n → π*	0	0	0	0
	5.01	0.012	B ₂	n → σ*	0	0	0	0
	5.31	0.077	A ₁	$\begin{pmatrix} \pi \rightarrow \pi^* \\ n \rightarrow \pi^* \end{pmatrix}$	0	0	0	0
	6.04	0.037	B ₂	n → σ*	0	0	0	0
	6.11	0.06	A ₁	n → σ*	0	0	0	0
	6.98	0.09	A ₁	n → σ*	0	0	0	0
	7.06	0.00	B ₂	n → σ _R *	6	29	64	99
	7.14	0.177	B ₂	$\begin{pmatrix} \sigma \rightarrow \sigma^* \\ n \rightarrow \sigma^* \end{pmatrix}$	0	0	0	0
	7.17	0.00	A ₂	n → σ*	0	0	0	0
	7.62	0.148	B ₂	$\begin{pmatrix} \sigma \rightarrow \sigma^* \\ n \rightarrow \sigma^* \end{pmatrix}$	0	0	0	0
	7.85	0.238	B ₂	$\begin{pmatrix} \pi \rightarrow \pi^* \\ n \rightarrow \pi^* \end{pmatrix}$	0	0	0	0
	7.96	0.375	A ₁	$\begin{pmatrix} \sigma \rightarrow \sigma^* \\ n \rightarrow \sigma^* \end{pmatrix}$	0	0	0	0

* [20]

b [19]

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

Molecule (symmetry)	MRINDO/S			
	Transition energy	Split	Symmetry of excited state	Type of transition
C ₃ H ₃ N ₃ (D _{3h})	2.81	0.39	E''	n → π*
	2.83	0.37	E''	n → π*
	3.13	0.09	A ₂ '	n → π*
	3.47	0.33	A ₂ '	n → π*
	3.57	1.63	A ₂ '	π → π*
C ₂ H ₂ N ₄ (D _{2h})	1.03	0.65	B _{3u}	n → π*
	1.95	1.51	B _{2u}	π → π*
	2.43	0.61	B _{2g}	n → π*
	2.45	1.11	A _u	n → π*
	2.52	0.91	B _{1g}	n → π*
CHN ₅ (C _{2v})	1.33	0.54	B ₁	n → π*
	2.13	0.29	A ₂	n → π*
	2.77	0.28	B ₁	n → π*
	2.81	0.66	A ₂	n → π*
	2.83	0.94	B ₂	π → π*

good agreement with experimental value of 14.6 eV, while the INDO value of 15.8 eV is too high.

Among the seven highest occupied orbitals of *s*-tetrizine the b_{1u} , a_g , b_{2u} , and b_{3g} are the in-plane nitrogen lone-pair orbitals, while the b_{3u} , b_{1g} , and b_{2g} are the three highest energy occupied π orbitals. The two lowest unoccupied molecular orbitals, a_u and b_{3u} , are both of type π^* . All this is consistent with experimental and INDO results, and with the results of the *ab initio* calculations listed by Scheiner and Schaefer [22]. The in-plane nitrogen lone-pair orbitals are associated with lower IP's in *s*-tetrizine than in *s*-triazine. This is attributed to the perturbation caused by a group of four 'line-pairs'. Spencer et al. [23] and Sundbom [24] assumed that the interaction between the different lone-pairs and carbons is small, so that a group of four lone-pairs with low IP's is formed. The lone-pair splitting of 1.06 eV is about three times less than the value calculated for *s*-triazine. The INDO calculation gives a similar result.

In pentazine the perturbation effect is rather large. We find two in-plane nitrogen lone-pair orbitals, b_1 and a_1 , before the $b_1(\pi)$ ionization. The lone-pair splitting of 0.73 eV is about five times less than the value calculated in *s*-triazine. We have not been able to find either experimental or theoretical values for comparison.

4.2. Singlet excitations

(i) *S*-triazine. The assignment for the first two $n \rightarrow \pi^*$ transitions, considering the degenerate transitions at 3.2 eV as a single transition, agrees with the INDO assignment but reverses the reported order; the $1_{E''}(n \rightarrow \pi^*)$ is observed and calculated to be 0.13 eV below the $1_{A_2}(n \rightarrow \pi^*)$. The $1_{A_2}(n \rightarrow \pi^*)$ transition

at 3.22 eV is in reasonable agreement with the reported value of 3.9 eV. This transition is strong and its calculated oscillator strength of 0.02 is in very good agreement with the reported value of 0.018.

Similar to benzene and other azabenzenes the three $\pi \rightarrow \pi^*$ transitions are calculated to be in the region below $63,000 \text{ cm}^{-1}$. These bands are centred at 5.20, 6.82, and 7.87 eV and seem to be correlated with the benzenoid bands $1_{B_{2u}}$, $1_{B_{1u}}$, and $1_{E_{1u}}$, respectively. The lowest $\pi \rightarrow \pi^*$ transition at 5.20 eV is in reasonable agreement with the reported value of 5.46 eV. However, this benzenoid band has been reported to be symmetry forbidden and it is probably because of this that the calculated oscillator strength is zero. In accordance with the symmetry forbiddenness, the reported value of 0.002 is small, being about the same size as in benzene itself. Unlike benzene, the second $1_{E'}(\pi \rightarrow \pi^*)$ transition at 6.82 eV is followed by almost equally intense component with a very small separation of 0.03 eV. This can be attributed to the perturbation caused by a group of three lone-pairs. We note a similar situation for the third $1_{E'}(\pi \rightarrow \pi^*)$ transition at 7.87 eV. This band is the most intense of all the bands in *s*-triazine. It is notable here that this strongest $\pi \rightarrow \pi^*$ transition is overlapped by a weak Rydberg transition with a large enough separation so that it is easy to distinguish between them. This is consistent with the observation of Fridh et al. [25].

Most of the bands in *s*-triazine are of valence-shell type, while a few show a very small percentage of Rydberg characters. The only $1_{E'}(n \rightarrow \sigma_R^*)$ transition at 7.29 eV shows appreciable Rydberg character of 85%. This band is very weak ($f = 0.002$). A quantum defect of 0.91 corresponding to the first IP (ionization potential) (e') suggests that this band is one of the members of *ns* Rydberg series. This is consistent with the observation of Fridh et al. [25] who suggested that the only possible Rydberg transitions that might overlap the intense $\pi \rightarrow \pi^*$ band at 7.79 eV are $6e' \rightarrow 3s$ and $1e'' \rightarrow 3s$.

(ii) *S-tetrazine*. A $1_{B_{3u}}(\pi \rightarrow \pi^*)$ transition is observed at 2.25 eV, the calculation also predicts that the lowest transition is $1_{B_{3u}}(n \rightarrow \pi^*)$ at 1.68 eV. The $\pi \rightarrow \pi^*$ band has an onset at 4.34 eV with E_{max} at 5.01 eV. The calculation indicates a $1_{B_{2u}}(\pi \rightarrow \pi^*)$ band at 3.46 eV which results in rather larger discrepancy with experiment of 25%. The INDO calculation gives somewhat better agreement with experimental values.

The reported second $1_{B_{3u}}(n \rightarrow \pi^*)$ state is theoretically difficult to investigate in *s*-tetrazine. The *ab initio* calculation [22] and the INDO calculation is not able to investigate the second $1_{B_{3u}}$ surface. Ghosh and Chowdhury have recently identified the analogous state for 3,6-diphenyl-*s*-tetrazine with band origin at 3.25 eV [26]. Additionally, Ha has predicted a vertical excitation energy of 5.10 eV for this state [27]. We note a $1_{B_{3u}}(n \rightarrow \pi^*)$ band at 5.23 eV which is in very good agreement with the predicted value of 5.10 eV.

Fridh et al. [18] investigated the electron impact energy loss spectrum of *s*-tetrazine. According to the theoretical studies, they assigned the valence $\pi \rightarrow \pi^*$ transitions as: $1_{B_{2u}}$, $1_{B_{1u}}$, $1_{B_{1u}}$, and $1_{B_{2u}}$ with maxima at 5.0, 7.1, 7.6 and 8.3 eV, respectively. This is consistent with our calculation. Furthermore, they suggest that the dominant energy absorption occurs around 8 eV. The main characteristic of *s*-tetrazine is that this peak is split into two peaks (at 7.6 eV and 8.3 eV), which appear to be approximately equal in strength. This is in very good agreement with the calculation. However the calculated splitting of 0.22 eV is less than the predicted value of 0.7 eV.

As to the Rydberg excitations, *s*-tetrazine shows two bands at 7.15 eV and 7.68 eV. In contrast to the situation for *s*-triazine, these bands are very weak. An oscillator strength of zero does indicate that such bands can be seen experimentally with stable experimental conditions.

The first Rydberg band, $1_{B_{2g}}(n \rightarrow \sigma_R^*)$, at 7.15 eV is associated with 92% Rydberg character. A quantum defect of 0.91 suggests this band to be a member of the *ns* Rydberg series. Fridh et al. [18] observe such bands in the higher energy region (12.26–12.49 eV) with quantum defect of 0.99. The second Rydberg band at 7.68 eV has a quantum defect of 0.71 which is too large for a *p* transition and too small for an *s* transition. The analysis of antibonding MO's indicates that the electrons are mainly upon the $3p$ orbitals of nitrogen atoms. Thus this band can be assigned $n \rightarrow 3p$. This agrees with the bands observed in the (7.1–7.7 eV) region [18].

(iii) *Pentazine*. Before the onset of $1_{B_2}(\pi \rightarrow \pi^*)$ we calculate four singlet $n \rightarrow \pi^*$ transitions, the lowest being $1_{B_1}(n \rightarrow \pi^*)$ at 1.87 eV. Contrary to the situations for *s*-triazine and *s*-tetrazine, none of these bands is strong.

Due to the presence of a relatively larger number of lone-pairs, numerous transitions corresponding to the promotion of these electrons can be expected. This will in turn affect the $\pi \rightarrow \pi^*$ spectrum of pentazine. This effect is pronounced in the present calculation. We note only one $1_{B_2}(\pi \rightarrow \pi^*)$ at 3.77 eV. It can be correlated with the benzenoid $1_{B_{2u}}$ band though it seems symmetry allowed, owing to its oscillator strength of 0.012. A $1_{A_1}(\pi \rightarrow \pi^*)$ transition at 5.31 eV is rather perturbed by the promotion of lone-pair electrons. Nevertheless, this band is a significant one owing to its oscillator strength of 0.077 and seems analogous to the benzenoid $1_{B_{1g}}$ band. The $1_{B_2}(\pi \rightarrow \pi^*)$ state at 7.85 eV is again perturbed by the promotion of lone-pairs, it is comparatively very strong, and can be correlated with the intense benzenoid band $1_{E_{1u}}$. The main characteristic of pentazine is that this strong $\pi \rightarrow \pi^*$ band is badly overlapped by the intense $\sigma_n \rightarrow \sigma^*$ type transitions on both of its ends.

The presence of a number of significant $\sigma_n \rightarrow \sigma^*$ type transitions in pentazine cannot be ignored in discussion. Transitions of this type are also present in *s*-triazine and *s*-tetrazine, but they are relatively very weak. In pentazine, the intensity of these bands increases towards shorter wave length with a maximum absorption occurring around 8 eV. The most prominent of them are centred at 7.14, 7.62, and 7.96 eV. It is notable here that the Rydberg band at 7.06 eV is overlapped by an intense $\sigma_n \rightarrow \sigma^*$ transition with a separation of 0.08 eV. Thus the perturbation caused by the promotion of 'lone-pairs' makes it difficult for the Rydberg band to be identified. Similarly, the strongest $\pi \rightarrow \pi^*$ at 7.85 eV is overlapped by $\sigma_n \rightarrow \sigma^*$ bands (at 7.62 eV and 7.96 eV). We note only one Rydberg transition at 7.06 eV which is associated with 99% Rydberg character. A quantum defect of 0.97 suggests this band is a member of the *ns* Rydberg series. We have not been able to find experimental or theoretical results for comparison.

4.3. Triplet excitations

All the transitions listed in Table 3 are of valence-shell type. The lowest triplet transition is assigned as $E''(n \rightarrow \pi^*)$ in *s*-triazine, $B_{3u}(n \rightarrow \pi^*)$ in *s*-tetrazine, and $B_1(n \rightarrow \pi^*)$ in pentazine. The corresponding S-T (singlet-triplet) splits are 0.39 eV

in *s*-triazine, 0.65 eV in *s*-tetrazine, and 0.54 eV in pentazine. Experimentally [28] the lowest singlet and triplet in *s*-tetrazine are reported at 2.25 eV and 1.69 eV, respectively with an S-T split of 0.56 eV. This is in reasonable agreement with the calculation. The first triplet $\pi \rightarrow \pi^*$ transition is calculated at 3.57 eV, 1.95 eV, and 2.83 eV in *s*-triazine, *s*-tetrazine, and pentazine, respectively. The corresponding S-T split of 1.63 eV, 1.51 eV, and 0.94 eV decreases with increasing perturbation.

5. Conclusion

Replacement of CH in benzene by $\geq N$: removes a CH bonding level and introduces a 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 azines is > 10 eV. The total populations in the azines based upon a Mulliken population analysis show that the nitrogen atoms are overall sp^2 hybridized. In the lone-pair orbitals the promotion of $2s$ to $2p$ varies sharply from molecule to molecule in the following order:

$$s\text{-triazine} < s\text{-tetrazine} < \text{pentazine}.$$

The substituent shows a very slow decrease in the first ionization potential and consequently the onset of the first Rydberg band in azines occurs in a very narrow region (7–7.12 eV). The calculation also reveals that the substituent shifts the frequencies of the benzenoid bands and alters their intensities somewhat. Thus benzene shows a lot of resistance to changing its π spectrum.

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Appendix A

CI matrix elements

In a CI calculation we need the matrix elements of the Hamiltonian H_e with respect to the ground and the different excited configurations. Here we give only the final expressions for such elements, considering only the singly excited configurations obtained by replacing the MO ψ_i in the ground-state determinant Φ_0 by the (virtual) MO ψ_a .

Diagonal elements:

$$\int \Phi_0 H_e \Phi_0 d\tau = E_0 = 2 \sum_{\text{occ}} H_i + \sum_{i,j}^{\text{occ}} (2J_{ij} - K_{ij}), \quad (\text{A.1})$$

$$\int {}^1\Phi_i^a (H_e - E_0) {}^1\Phi_i^a d\tau = \epsilon_a - \epsilon_i - J_{ia} + 2K_{ia}, \quad (\text{A.2})$$

and

$$\int {}^3\Phi_i^a (H_e - E_0) {}^3\Phi_i^a d\tau = \epsilon_a - \epsilon_i - J_{ia}, \quad (\text{A.3})$$

where

$$H_i = (i|H|i).$$

Off-diagonal elements:

$$\int^1 \Phi_j^a H_e^1 \Phi_j^b d\tau = (a|H|b) + \sum_i^{\text{occ}} \{2(ii|ab) - (ib|ai)\} - (jj|ab) + 2(jb|aj), \quad (\text{A.4})$$

$$\int^3 \Phi_j^a H_e^3 \Phi_j^b d\tau = \int^1 \Phi_j^a H_e^1 \Phi_j^b d\tau - 2(jb|aj), \quad (\text{A.5})$$

$$-\int^1 \Phi_j^a H_e^1 \Phi_k^a d\tau = (j|H|k) + \sum_i^{\text{occ}} \{2(ii|jk) - (ik|ji)\} + (aa|kj) - 2(aj|ka), \quad (\text{A.6})$$

$$\int^3 \Phi_j^a H_e^3 \Phi_k^a d\tau = \int^1 \Phi_j^a H_e^1 \Phi_k^a d\tau - 2(aj|ka), \quad (\text{A.7})$$

$$\int^1 \Phi_j^a H_e^1 \Phi_k^b d\tau = 2(aj|kb) - (ab|kj), \quad (\text{A.8})$$

and

$$\int^3 \Phi_j^a H_e^3 \Phi_k^b d\tau = -(ab|kj). \quad (\text{A.9})$$

Appendix B

Molecular integrals in the MRINDO/S approximations

$$\begin{aligned} (i|H|j) &= \sum_{\mu,\nu} C_{\mu i} C_{\nu j} (\mu|H|\nu) \\ &= \sum_A \sum_{n_1}^A \sum_{\mu}^{A,n_1} \left\{ \left(U_{\mu\mu} - \sum_{(B \neq A)} Z_B \Gamma_{n_1(A)n_2(B)} \right) C_{\mu i} C_{\nu j} \right. \\ &\quad \left. + \sum_B \sum_{n_2}^B \sum_{\nu \neq \mu}^{B,n_2} C_{\mu i} C_{\nu j} \beta_{n_1(A)n_2(B)}^{\circ} S_{\mu\nu} \right\}, \end{aligned} \quad (\text{B.1})$$

$$\begin{aligned} (ij|kl) &= \sum_{\mu,\nu,\lambda,\sigma} C_{\mu i} C_{\nu j} C_{\lambda k} C_{\sigma l} (\mu\nu|\lambda\sigma) \\ &= \sum_A \sum_{n_1 \neq n_2}^A \sum_{\mu}^{A,n_1} \sum_{\lambda}^{A,n_2} C_{\mu i} C_{\nu j} C_{\lambda k} C_{\sigma l} \Gamma_{n_1(A)n_2(A)} \\ &\quad + \sum_{B \neq A} \sum_{n_1}^A \sum_{n_2}^B \sum_{\mu}^{A,n_1} \sum_{\lambda}^{B,n_2} C_{\mu i} C_{\nu j} C_{\lambda k} C_{\sigma l} \Gamma_{n_1(A)n_2(B)} \\ &\quad + \sum_A \sum_{n_1}^A \sum_{\mu}^{A,n_1} \left[C_{\mu i} C_{\nu j} C_{\mu k} C_{\mu l} (\mu\mu|\mu\mu) + \sum_{\lambda \neq \mu}^{A,n_1} \{ C_{\mu i} C_{\nu j} C_{\lambda k} C_{\sigma l} (\mu\mu|\lambda\lambda) \right. \\ &\quad \left. + C_{\mu i} C_{\lambda j} C_{\mu k} C_{\sigma l} (\mu\lambda|\mu\lambda) + C_{\mu i} C_{\lambda j} C_{\lambda k} C_{\sigma l} (\mu\lambda|\lambda\mu) \right], \end{aligned} \quad (\text{B.2})$$

where the last line is true for s, p, \dots orbitals only.

References

1. Pople JA (1953) *Trans Faraday Soc* 49:1375
2. Pariser R, Parr RG (1953) *J Chem Phys* 21:466; (1953) 21:767
3. a. Pople JA, Santry DP, Segal GA (1965) *J Chem Phys* 43:S129
b. Pople JA, Segal GA (1965) *J Chem Phys* 43:S136
c. Pople JA, Segal GA (1966) *J Chem Phys* 44:3289
4. Pople JA, Beveridge DL, Dobosh PA (1967) *J Chem Phys* 47:2026
5. Del Bene J, Jaffe HH (1968) *J Chem Phys* 48:1807; (1968) 48:4050
6. Del Bene J, Jaffe HH (1969) *J Chem Phys* 50:1126
7. Krogh-Jespersen K, Ratner M (1976) *J Chem Phys* 65:1305
8. Salahub DR, Sandorfy C (1971) *Theor Chim Acta* 20:227
9. Singh AN, Haque W (1977) *Indian J Phys* 51B:218
10. Singh AN, Prasad RS (1980) *Chem Phys* 49:267
11. Prasad RS, Roy CP (1987) *Indian J Phys* 61B:330
12. Pople JA, Beveridge DL (1970) *Approximate molecular orbital theory*. McGraw-Hill, New York
13. Parr RG (1952) *J Chem Phys* 20:1499
14. Mulliken RS, Rieke CA, Orloff D, Orloff H (1949) *J Chem Phys* 17:1248
15. Mulliken RS (1952) *J Chem Phys* 56:295
16. Koopmans T (1933) *Physica* 1:104
17. Robin MB, Kuebler NA, Brundle CR (1972) In: Shirley DA (ed) *Electron spectroscopy*. North-Holland, Amsterdam London, pp 370–373
18. Fridh C, Asbrink L, Jonsson BO, Lindholm E (1972) *Int J Mass Spectrum Ion Phys* 9:485
19. Ridley J, Zerner M (1973) *Theor Chim Acta* 32:111
20. Innes KK, Byrne JP, Ross IG (1967) *J Mol Spectros* 22:125
21. Gleiter R, Heilbronner E, Hornung V (1970) *Angew Chem Int Ed Eng* 9:901
22. Scheiner AC, Schaefer III HF (1987) *J Chem Phys* 87:3539
23. Spencer GH, Cross PC, Wiberg KB (1961) *J Chem Phys* 35:1925
24. Sundbom M (1971) *Acta Chem Scand* 25:487
25. Fridh C, Asbrink L, Jonsson BO, Lindholm E (1972) *Int J Mass Spectrum Ion Phys* 8:85
26. Ghosh S, Chowdhury M (1982) *Chem Phys Lett* 85:233
27. Ha TK (1975) *Mol Phys* 29:1829
28. Mason SF (1959) *J Chem Soc* 1263