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

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Abstract. An MRINDO/S calculation completed by singly excited configuration interaction was performed on the azines *vic*-triazine, *as*-triazine, *vic*-tetrazine, and *as*-tetrazine. The importance of outer (Rydberg) atomic orbitals is stressed and it is found that a few transitions of these azines lead to an excited state with considerable Rydberg character. Ionization potentials of the azines are also interpreted.

Key words: Spectroscopic MRINDO/S – *vic*-Triazine – *as*-Triazine – *vic*-Tetrazine *as*-Tetrazine

1 Introduction

The π-π states of azines have been the subject of several calculations mostly within the framework of molecular orbital (MO) theory, with or without self-consistent-field (SCF) refinements [1–5]. The π-π states are basically perturbed benzene states, and generally the theoretical picture is fairly satisfactory. The same cannot be said of the n-π states.

The experimental benchmarks in all these calculations are the separations between the lowest singlet π-π and n-π states, the separations between the lowest singlet and triplet n-π states, and the intensities of allowed singlet n → π transitions.

The electronic spectra of *s*-triazine and *s*-tetrazine have been studied theoretically and experimentally by several workers [6–13]; however, the literature is scarce regarding spectra of their isomers, viz. *vic*-triazine, *as*-triazine, *vic*-tetrazine, and *as*-tetrazine. Pukanic et al. [14] considered these isomers but restricted their calculations to π electrons only. They could not interpret n-π states and Rydberg transitions occuring in the spectra of these isomers.

The present method has been applied to various small molecular species with encouraging results [15, 16]. In a previous publication [10] we interpreted the observed spectra of *s*-triazine, *s*-tetrazine, and pentazine. In the present investigation, the electronic spectra of *vic*-triazine, *as*-triazine, *vic*-tetrazine, and *as*-tetrazine have been calculated. Agreement with the results listed by Pukanic et al. [14] is good. In addition, we interpret n-π states and Rydberg transitions of these isomers. The computed results are also compared with the observed spectrum of benzene.

The geometry for the bond lengths of these azines has been taken from Pukanic et al. [14]. Each molecule was taken to be planar and reasonable bond angles were chosen to give the appropriate dimensions.

2 Outline of the work

In the MRINDO/S method we added Slater atomic orbitals to the basis H2*s*, H2*p*, C3*s*, C3*p*, N3*s* and N3*p*. The details of the method can be found in Ref. [10]. Throughout this work we have used the same basis set and the same parameters on the grounds that this is more likely to disclose trends in the computed properties of these azines.

The energy of the ground state was first minimized in the usual way. Configuration interaction was applied including the lowest 30 singly excited configurations for both singlets and triplets. Jacobi diagonalization iterations were continued until all off-diagonal elements were smaller than 10^{-4} a.u. and the SCF procedure was terminated when all eigenvalues agreed within 10^{-3} a.u. between successive iterations.

3 Results

The Koopmans theorem [17] ionization potentials (IPs) and the corresponding orbital symmetries are listed in Table 1. The theoretical values for the IPs given in the first columns were taken from Pukanic et al. [14].

The lower singlet–singlet excitation energies, oscillator strengths, and symmetries of the excited states are given in Table 2. The theoretical values listed by Pukanic et al. [14] are given in the first columns. The last columns

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

Molecule (Symmetry)	PPP [14]			MRINDO/S		
	IP 1	Symmetry of orbital 2	Type 3	IP 4	Symmetry of orbital 5	Type 6
vic-Triazine (C_{2v})	10.61			10.54	b_2	σ,n
				10.71	a_2	π
				11.03	a_1	σ,n
				11.24	b_1	π
				12.62	a_1	σ
				14.05	b_2	σ
				14.50	b_1	π
as-Triazine (C_s)	10.32			10.33	a'	σ,n
				10.81	a''	π
				11.39	a''	π
				11.62	a'	σ,n
				12.00	a'	σ,n
				14.24	a'	σ
				14.98	a''	π
vic-Tetrazine (C_{2v})	10.88			10.39	a_1	σ,n
				10.99	b_1	π
				11.29	b_2	σ,n
				11.59	a_2	π
				12.38	b_2	σ,n
				12.81	a_1	σ
				14.90	b_1	π
as-Tetrazine (C_{2v})	11.07			10.35	b_2	σ,n
				10.71	b_2	σ,n
				10.96	a_2	π
				11.63	b_1	π
				12.08	a_1	σ,n
				14.30	a_1	σ
				14.75	b_1	π

of Table 2 contain the percentages of Rydberg character of the excited states. The transition energies, the symmetries of the excited states, and the splittings of the five lowest singlet–triplet transitions of each molecule are given in Table 3. The percentages of the Rydberg character for all these triplet states are zero and hence are not cited in Table 3 for clarity. The first columns of Table 3 contain results listed by Pukanic et al. [14]. A comparative list of the singlet $\pi \rightarrow \pi^*$ transitions in the four azines under the MRINDO/S approximation is provided in Table 4.

The results are compared mostly with the theoretical values cited in Tables 1–3; otherwise references are noted.

4 Discussion

4.1 Ionization potentials

The first IP of all four azines is interpreted as the removal of an electron from an in-plane lone-pair orbital. The separations between the first two lone-pair orbitals in *vic*-triazine and *as*-triazine are 0.49 and 1.29 eV, respectively. These separations are very low compared with the corresponding separation in *s*-triazine of about 3.25 eV given in a review by Innes et al. [11] and of about 3.5 eV under the MRINDO/S approximation [10]. The calculated separation, 1.29 eV, for *as*-triazine is comparable with the separation found in diazine [18]; however, the calculated low separations can be attributed to the reduction in symmetry. The lone-pair splitting in *vic*-tetrazine and *as*-tetrazine is calculated to be low compared with the splitting in *vic*-triazine and *as*-triazine. A similar trend is predicted for *s*-triazine and *s*-tetrazine under the MRINDO/S and INDO approximations [7, 10] and also in a review by Innes et al. [11]. Pukanic et al. [14] did not interpret this aspect of occupied orbitals. However, we note that our calculated first IPs of all the azines and the values listed by Pukanic et al. are comparable. In addition, the first IP of *as*-triazine (10.33 eV) is in fair agreement with the value (9.61 eV) cited in Ref. [11]. Thus our calculation shows no great deviation and hence seems to be in the right direction. The calculated first IP of the azines follows the order *as*-triazine < *as*-tetrazine < *vic*-tetrazine < *vic*-triazine. The lowest unoccupied MO in all four azines is π^*.

4.2 Singlet excitations

4.2.1 vic-Triazine

We note three n $\rightarrow \pi^*$ transitions before the onset of the $\pi \rightarrow \pi^*$ transition. None of these transitions show intensity. In ethanol a shoulder at 325 nm (about 3.81 eV) and a peak with ε(max) = 860 at 288 nm (about 4.3 eV) are found. Hence the possibility of two resolved n, π^* states is expected in *vic*-triazine [11]. However, we predict an n $\rightarrow \pi^*$ transition at 3.95 eV which seems to be forbidden (f = 0.00) but which lies within the expected region of energy [11].

We report six $\pi \rightarrow \pi^*$ transitions in the region below 63000 cm^{-1}. Three of these bands centred at 5.44, 6.48, and 7.86 eV seem to be correlated with the benzenoid bands $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$, respectively. In contrast to *s*-triazine [10, 12, 13], we note two $\pi \rightarrow \pi^*$ transitions before the first benzenoid band at 5.44 eV. The calculated band at 5.44 eV is in reasonable agreement with the reported band at 5.18 eV, but the calculated band seems relatively more intense (f = 0.076). Unlike benzene, the second band at 6.48 eV is followed by a relatively less intense component with a separation of 0.59 eV. A similar situation, but with very low separation (about 0.03 eV), is found in *s*-triazine [10]. However, Fluscher et al. [12] predict two $\pi \rightarrow \pi^*$ transitions in *s*-triazine at 8.08 and 8.70 eV, the former being dipole-forbidden. The main characteristic of *vic*-triazine is that the third band shows a peak, not the dominant one, which splits into two peaks (at 7.86 and 8.16 eV) with varied strength. These peaks are approximately equal in strength in *s*-triazine and *s*-tetrazine [6, 10]. In addition, that the splitting is larger than in other azines is in agreement with theoretical studies [1, 6, 11, 19]. In *vic*-triazine the presence of the $^1B_2$ ($\pi \rightarrow \pi^*$) band is indicated [11] but the energy region is not mentioned. The lowest singlet π-π and n-π states are separated by 1.19 eV. This separation in *s*-triazine comes to be 1.73 eV from experiment [12].

Table 2. Lowest singlet–singlet transitions in azines. All energies are in electron volts

Molecule (Symmetry)	PPP [14]			MRINDO/S				% Rydberg character			
	Transition energy 1	f 2	Type of transition 3	Transition energy 4	f 5	Symmetry of excited state 6	Type 7	H 8	C 9	N 10	Total 11
vic-Triazine (C_{2v})	5.18	0.001	$\pi \rightarrow \pi^*$	2.65	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
	6.28	0.065	$\pi \rightarrow \pi^*$	3.18	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
	7.27	1.253	$\pi \rightarrow \pi^*$	3.36	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
	7.30	1.072	$\pi \rightarrow \pi^*$	3.84	0.006	B_2	$\pi \rightarrow \pi^*$	0	0	0	0
				3.95	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
				4.36	0.013	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				4.92	0.000	A_2	$\sigma \rightarrow \pi^*$	0	0	0	0
				5.19	0.000	B_1	$\sigma \rightarrow \pi^*$	0	0	0	0
				5.37	0.078	B_2	$n \rightarrow \sigma^*$	1	2	0	3
				5.44	0.076	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				5.90	0.000	A_2	$\pi \rightarrow \sigma^*$	1	1	0	2
				6.25	0.000	B_1	$\pi \rightarrow \sigma^*$	0	0	0	0
				6.39	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				6.48	0.100	B_2	$\pi \rightarrow \pi^*$	0	0	0	0
				6.58	0.051	A_1	$n \rightarrow \sigma^*$	1	2	0	3
as-Triazine (C_s)	5.02	0.126	$\pi \rightarrow \pi^*$	2.20	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
	6.45	0.066	$\pi \rightarrow \pi^*$	3.25	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
	7.34	0.995	$\pi \rightarrow \pi^*$	3.37	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
	7.67	1.197	$\pi \rightarrow \pi^*$	3.70	0.035	A'	$\pi \rightarrow \pi^*$	0	0	0	0
				3.91	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
				4.62	0.014	A'	$\pi \rightarrow \pi^*$	0	0	0	0
				5.12	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
				5.17	0.006	A'	$n \rightarrow \sigma^*$	0	0	0	0
				5.63	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
				5.73	0.136	A'	$\pi \rightarrow \pi^*$	0	0	0	0
				6.08	0.000	A''	$\pi \rightarrow \sigma^*$	0	0	0	0
				6.16	0.025	A'	$n \rightarrow \sigma^*$	0	1	0	1
				6.18	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
				6.39	0.015	A'	$\pi \rightarrow \pi^*$	1	3	1	5
				6.52	0.000	A''	$\pi \rightarrow \sigma^*$	0	1	0	1
vic-Tetrazine (C_{2v})	5.17	0.047	$\pi \rightarrow \pi^*$	2.43	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
	6.41	0.072	$\pi \rightarrow \pi^*$	2.53	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
	7.43	1.104	$\pi \rightarrow \pi^*$	3.27	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
	7.51	1.178	$\pi \rightarrow \pi^*$	3.38	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				3.76	0.007	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				4.13	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				4.41	0.008	B_2	$\pi \rightarrow \pi^*$	0	0	0	0
				4.84	0.000	A_2	$\sigma \rightarrow \pi^*$	0	0	0	0
				4.91	0.000	B_1	$\sigma \rightarrow \pi^*$	0	0	0	0
				4.97	0.040	B_2	$\pi \rightarrow \pi^*$	0	0	0	0
				5.13	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
				5.39	0.130	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				6.09	0.008	B_2	$n \rightarrow \sigma^*$	0	0	0	0
				6.12	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				6.24	0.000	A_2	$\pi \rightarrow \sigma^*$	0	0	0	0
as-Tetrazine (C_{2v})	5.22	0.048	$\pi \rightarrow \pi^*$	2.27	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
	6.63	0.002	$\pi \rightarrow \pi^*$	2.56	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
	7.48	1.138	$\pi \rightarrow \pi^*$	2.97	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
	7.52	1.146	$\pi \rightarrow \pi^*$	3.40	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
				3.57	0.000	B_1	$n \rightarrow \pi^*$	0	0	0	0
				3.65	0.020	B_2	$\pi \rightarrow \pi^*$	0	0	0	0
				4.59	0.003	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				4.99	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				5.01	0.029	A_1	$\pi \rightarrow \pi^*$	0	0	0	0
				5.17	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				5.25	0.058	B_2	$\pi \rightarrow \pi^*$	0	1	0	1
				5.54	0.000	A_2	$n \rightarrow \pi^*$	0	0	0	0
				6.09	0.035	A_1	$n \rightarrow \sigma^*$	0	1	0	1
				6.17	0.000	A_2	$\pi \rightarrow \sigma^*$	1	1	0	2
				6.53	0.069	B_2	$\pi \rightarrow \pi^*$	0	0	0	0

Table 3. The five lowest singlet–triplet transitions in azines. All energies are in electron volts

Molecule (Symmetry)	PPP [14]		MRINDO/S			
	Transition energy	Type of transition	Transition energy	Split	Symmetry of excited state	Type of transition
vic-Triazine (C_{2v})	3.30	$\pi \rightarrow \pi^*$	2.06	2.30	A_1	$\pi \rightarrow \pi^*$
	4.08	$\pi \rightarrow \pi^*$	2.11	0.54	B_1	$n \rightarrow \pi^*$
	4.19	$\pi \rightarrow \pi^*$	2.33	1.62	B_1	$n \rightarrow \pi^*$
	4.85	$\pi \rightarrow \pi^*$	2.81	1.03	B_2	$\pi \rightarrow \pi^*$
			2.92	0.44	A_2	$n \rightarrow \pi^*$
as-Triazine (C_s)	3.33	$\pi \rightarrow \pi^*$	1.59	0.61	A''	$n \rightarrow \pi^*$
	3.51	$\pi \rightarrow \pi^*$	2.22	2.40	A'	$\pi \rightarrow \pi^*$
	4.28	$\pi \rightarrow \pi^*$	2.51	1.19	A'	$\pi \rightarrow \pi^*$
	5.81	$\pi \rightarrow \pi^*$	2.63	0.62	A''	$n \rightarrow \pi^*$
			2.66	0.71	A''	$n \rightarrow \pi^*$
vic-Tetrazine (C_{2v})	3.32	$\pi \rightarrow \pi^*$	1.80	0.63	B_1	$n \rightarrow \pi^*$
	3.83	$\pi \rightarrow \pi^*$	2.00	0.53	A_2	$n \rightarrow \pi^*$
	4.19	$\pi \rightarrow \pi^*$	2.36	2.05	B_2	$\pi \rightarrow \pi^*$
	5.31	$\pi \rightarrow \pi^*$	2.57	0.70	B_1	$n \rightarrow \pi^*$
			2.86	0.90	A_1	$\pi \rightarrow \pi^*$
as-Tetrazine (C_{2v})	3.46	$\pi \rightarrow \pi^*$	1.78	0.49	A_2	$n \rightarrow \pi^*$
	3.95	$\pi \rightarrow \pi^*$	1.96	0.60	A_2	$n \rightarrow \pi^*$
	4.37	$\pi \rightarrow \pi^*$	2.46	1.19	B_2	$\pi \rightarrow \pi^*$
	5.51	$\pi \rightarrow \pi^*$	2.54	1.03	B_1	$n \rightarrow \pi^*$
			2.80	2.21	A_1	$\pi \rightarrow \pi^*$

Table 4. $\pi \rightarrow \pi^*$ transitions in azines under MRINDO/S

MRINDO/S							
vic-Triazine		*as*-Triazine		*vic*-Tetrazine		*as*-Tetrazine	
ΔE	f	ΔE	f	ΔE	f	ΔE	f
3.84	0.006	3.70	0.035	3.76	0.007	3.65	0.020
4.36	0.013	4.62	0.014	4.41	0.008	4.59	0.003
5.44	0.076	5.73	0.136	4.97	0.040	5.01	0.029
6.48	0.100	6.39	0.015	5.39	0.130	5.25	0.058
7.07	0.014	7.08	0.002	6.64	0.048	6.53	0.069
7.86	0.157	7.55	0.054	7.44	0.150	7.96	0.454
8.18	0.239	7.61	0.465	–	–	–	–
–	–	7.82	0.043	–	–	–	–
–	–	8.24	0.052	–	–	–	–

The presence of $n \rightarrow \sigma^*$ transitions cannot be ignored in the discussion. We note five $n \rightarrow \sigma^*$ transitions amongst the one at 7.79 eV is the most intense of all the bands in the spectrum of *vic*-triazine. Thus the dominant energy absorption occurs around 8 eV. This is also the case in other azines [1, 6, 14] and benzene [20]. All the $n \rightarrow \sigma^*$ transitions originate from an in-plane lone-pair orbital.

As to the Rydberg excitations, we report three Rydberg bands in *vic*-triazine. The first at 7.55 eV possesses a quantum defect of 0.90. Thus this band is one of the members of the *ns* Rydberg series. This band, as compared with the other two, is intense ($f = 0.049$) and can be detected experimentally under stable experimental conditions. This requirement seems essential because this band is overlapped by relatively more intense ($n \rightarrow \sigma^*$) transitions at both of its ends. A second member of the *ns* Rydberg series with a quantum defect of 0.81 appears at 7.71 eV: this is very weak ($f = 0.00$). The third Rydberg band at 8.6 eV is very weak and is badly overlapped by intense $\pi \rightarrow \pi^*$ bands at both of its ends. Thus its experimental detection seems to be rather difficult. This band with cent per cent Rydberg character possesses a quantum defect of 0.66 which seems to be too large for a *p* transition and too small for an *s* transition; however, the analysis of the antibonding MO indicates that the major electron population is in the 3*p* atomic orbitals of the carbon and nitrogen atoms. Thus this band corresponds to the first member of the *np* Rydberg series.

4.2.2 *as-Triazine*

Similar to *vic*-triazine, we note three $n \rightarrow \pi^*$ transitions in *as*-triazine before the onset of the $\pi \rightarrow \pi^*$ transition. None of these transitions show intensity; however, in methanol the spectrum of *as*-triazine consists of an $n \rightarrow \pi^*$ transition with ε(max) = 400 [11]. Reference [11] does not uncover the other details about this transition.

The π spectrum of *as*-triazine seems somewhat different from that of *vic*-triazine. The three benzenoid bands can be compared with the bands calculated at 5.73, 6.39, and 7.61 eV, respectively. The first band at 5.73 eV in *as*-triazine is more intense than the corresponding band in *vic*-triazine. The second band at 6.39 eV is split into three components, instead of two as in *vic*-triazine, with variable strength. Similarly, the third band at 7.61 eV splits into three fragments with a maximum separation of 0.63 eV; however, the band at 7.61 eV exhibits the far more dominant peak in the spectrum of *as*-triazine. This region of energy corresponds to the maximum energy absorption region. Thus the maximum absorption in *vic*-triazine and *as*-triazine occurs approximately in the same energy region but a difference exists that the maximum absorbing band in *vic*-triazine is n $\rightarrow \sigma^*$ while that in *as*-triazine is $\pi \rightarrow \pi^*$; however, a $\pi \rightarrow \pi^*$ transition with ε(max) = 3020 is reported in the spectrum of *as*-triazine [11]. The other details of the band remain covered. The lowest singlet π-π and n-π states are separated by about 1.5 eV. However, our calculated results are in reasonable agreement with the results listed by Pukanic et al., but we note a large deviation in the intensity of the bands. We are unable to predict such high intensities.

We note a number of n $\rightarrow \sigma^*$ type transitions in *as*-triazine. All these transitions are more or less intense, for the orbital of departure and the orbital of arrival both have the same orbital symmetry.

As to the Rydberg excitations, we note two Rydberg bands in the spectrum of *as*-triazine. The first band at 7.21 eV with 99% Rydberg character possesses a quantum defect of 0.92: thus this band forms the first member of the *ns* Rydberg series. The second Rydberg band at 7.60 eV has a quantum defect of 0.77. The analysis of the Rydberg MO indicates that this band corresponds to a member of the *np* Rydberg series. These two Rydberg bands are very weak (f = 0.00) and their experimental detection seems difficult on the ground that they are weak and that the first band lies in the vicinity of an intense n $\rightarrow \sigma^*$ band at 7.24 eV and the second one is overlapped by the intense $\pi \rightarrow \pi^*$ transitions at both of its ends.

4.2.3 vic-Tetrazine

In *vic*-tetrazine we report four n $\rightarrow \pi^*$ transitions before the onset of the $\pi \rightarrow \pi^*$ transition: none of these exhibit intensity. Such transitions are also reported in the shorter wavelength side of the spectrum but none exhibit oscillator strength.

The number of $\pi \rightarrow \pi^*$ transitions in *vic*-tetrazine is reduced. This can be attributed to the promotion of a group of four lone-pair atoms. The benzenoid band at 5.39 eV is succeeded by its less intense component at 4.97 eV. This situation is not found in *vic*-triazine and *as*-triazine. Furthermore, in contrast to the spectra of *vic*-triazine and *as*-triazine, the second and third bands at 6.64 and 7.44 eV, respectively, do not show splitting. The third band, being the most intense among the $\pi \rightarrow \pi^*$ transitions seems to be not very dominant. The most dominant transition is predicted at 8.15 eV with an oscillator strength of 0.405 and is assigned as n $\rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$. Thus the maximum energy absorption occurs around 8.0 eV, which is in agreement with the region in benzene [20]. Pukanic et al. predict the maximum absorption in *vic*-tetrazine at 7.51 eV. The lowest singlet π-π and n-π states in *vic*-tetrazine are separated by about 1.33 eV. We are unable to find theoretical or experimental results for comparison.

We predict only one Rydberg transition in *vic*-tetrazine at 7.34 eV with an oscillator strength of 0.001. This Rydberg band has a quantum defect of 1.04 and thus forms the first member of the *ns* Rydberg series. This band appears in the vicinity of an intense $\pi \rightarrow \pi^*$ transition with a separation of about 0.10 eV: however, a Rydberg band with a quantum defect δ = 0.95 is measured in *s*-tetrazine by electron impact [6].

4.2.4 as-Tetrazine

The π spectrum of *as*-tetrazine resembles the spectrum of *vic*-tetrazine, but in the case of *as*-tetrazine, the third benzenoid band at 7.96 eV is the most intense of all the transitions. Thus maximum absorption occurs around 8.0 eV. The n $\rightarrow \sigma^*$ type transitions seem less dominant than the $\pi \rightarrow \pi^*$ transitions in *as*-tetrazine. The lowest π-π and n-π states in *as*-tetrazine are separated by about 1.38 eV, which is very close to the corresponding separation in *vic*-tetrazine.

As in *vic*-tetrazine, we note only one Rydberg transition in *as*-tetrazine. This band at 7.27 eV has a quantum defect of 0.90 and thus forms the first member of the *ns* Rydberg series. It is noticeable that, in contrast to *vic*-tetrazine, this Rydberg band is very weak (f = 0.00) and lies around an intense n $\rightarrow \sigma^*$ type transition.

4.3 Triplet excitations

We assign the lowest state as an n-π state in these azines, except in *vic*-triazine where it is a π-π state. The singlet–triplet splittings of the $\pi \rightarrow \pi^*$ transitions show large deviation, while those of n $\rightarrow \pi^*$ transitions show near constancy in these azines. The separations between the lowest singlet n-π and triplet n-π states in *vic*-triazine, *as*-triazine, *vic*-tetrazine, and *as*-tetrazine are 0.54, 0.61, 0.63, and 0.49 eV, respectively. Besides the two triplet $\pi \rightarrow \pi^*$ transitions cited in Table 3, we predict other $\pi \rightarrow \pi^*$ transitions in the spectra of these azines. The energy regions for these transitions are as follows.
vic-Triazine: 3.42, 5.19, 5.69, and 7.53 eV
as-Triazine: 3.46, 5.17, 5.66, and 7.78 eV
vic-Tetrazine: 2.97, 3.79, 5.36, and 5.95 eV
as-Tetrazine: 3.33, 4.27, 5.35, and 5.79 eV
Thus our calculation and the calculation made by Pukanic et al. are comparable.

5 Conclusion

None of the n $\rightarrow \pi^*$ transitions in the azines show intensity. The reason might be due to the assignment of nonbonding orbitals, especially the out-of-plane orbitals (π orbitals). In a π orbital, which is responsible for originating excitations, a considerable nonbonding, though very much less than bonding character, is found. If, however, such an orbital is assigned as a lone-pair orbital, the n $\rightarrow \pi^*$ transition would have exhibited some intensity. Thus, a more sophisticated method is needed to meet the requirement. According to the present calculation it is obvious that benzene shows a lot of resistance to changing its π spectrum.

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