Semi-empirical Parameters in π-Electron Systems

XI. Calculations of the Electronic Structure of some Nitrogen Heterocycles Including π-Electrons and σ Lone Pairs

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A modified Pariser-Parr-Pople method has been extended to nitrogen heterocycles containing more than one sigma lone pair, n.

Bond distances, n and π ionization potentials and electronic transitions of $\pi - \pi^*$ and $n - \pi^*$ types have been calculated. The calculated results are compared with experimental data and other theoretical results.

I. INTRODUCTION

In previous papers of the present series [1-10] a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation has been evaluated. These parameters have been useful in the study of large organic molecules, for which all electron non-empirical calculations today are not possible. Together with the π-electrons the loosest bound σ-electrons, the lone pairs, n, are responsible for most of the chemical activity of organic molecules. The approach to extend the PPP method by taking lone pair electrons explicitly into account was introduced by Anno and co-workers.[11-13] In a recent work, Hohlneicher and Sänger [14] have also used this approach in a study of carbonyl and aza compounds.

Parameters for azines with one sigma lone pair have been presented in a previous paper.[3] These parameters have been used in a study of the porphin and copper porphin molecules.[15,16] The present investigation is an extension of this scheme to include lone pair (n) parameters in nitrogen containing molecules with more than one sigma lone pair.

The n parameters have been determined through a least squares fit to experimental data of pyridine, pyridazine, pyrimidine, and pyrazine. The finally adopted parameter values have then been applied in calculations on a set of molecules: *sym*-triazine, *sym*-tetrazine, phthalazine, cinnoline, quinazoline, quinoxaline, 1,5-naphthpyridine, phenazine, 9,10-diazaphenanthrene, imidazole, 9H-purine, and 7H-purine.

Although this method contains several approximations, described in detail in Section II, the results of the present investigation show a good overall agreement with available experimental results. The method can, for instance, be used for interpretation of photoelectron spectroscopy data and for prediction of $n - \pi^*$ transitions.

II. METHOD AND DETERMINATION OF PARAMETERS

The method was introduced in the first paper of this series.[1] It is essentially a SCF $-$ MO $-$ LCAO $-$ CI method in the Pariser-Parr-Pople approximation, formally implying zero-differential overlap (ZDO) and semi-empirical determination of some integrals.

The self-consistent field molecular orbitals have been evaluated by means of a computer program, SCF $-$ OPSZDO, written by B. Roos and M. Sundbom. This program also calculates the energy levels of excited states by mixing all configurations obtained from single excitations. The computer IBM 360/75 at Stockholms Datacentral has been used for the present calculation.

1. π Systems without inclusion of sigma lone pairs. The scheme applied for the evaluation of the semi-empirical π parameters and notations and equations used for the evaluation of the various integrals have been presented in previous papers [1-10] and will not be repeated here.

2. π Systems with inclusion of sigma lone pairs, n. In the present investigation, n parameters for azines have been included in the scheme. Identified lone pair ionization potentials and singlet $n - \pi^*$ transitions have been used as experimental conditions. The previously determined π parameters have been considered as fixed.

The n parameters are not necessarily defined as matrix elements between atomic orbitals, but can equally well be defined by means of delocalized orbitals. In order to account for delocalization, three different resonance integrals: $\beta_{N(n)N'(n)}$ (*ortho*), $\beta_{N(n)N'(n)}$ (*meta*), and $\beta_{N(n)N'(n)}$ (*para*) have been introduced. For the determination of two-electron integrals, the following approximation was made. The n orbitals were considered as localized orbitals. In order to get an indication of the limitations of this approach, two different hybridizations were assumed: namely (I) an sp^2 hybrid, and (II) a hybrid with 10 % s character.

The diagonal elements of the core operator, $\alpha_{\mu(\pi)}$ and $\alpha_{\mu(n)}$ are expressed as:

$$\alpha_{\mu(\pi)} = W_{\mu(\pi)} - 2\gamma_{\mu(\pi)\mu(n)} + K_{\mu(\pi)\mu(n)} - \sum_{\nu \neq \begin{cases} \mu(\pi) \\ \text{and} \\ \mu(n) \end{cases}} n_\nu \gamma_{\mu(\pi)\nu} \qquad (1)$$

$$\alpha_{\mu(n)} = W_{\mu(n)} - \gamma_{\mu(n)\mu(n)} - \gamma_{\mu(n)\mu(\pi)} + \tfrac{1}{2}K_{\mu(\pi)\mu(n)} - \sum_{\nu \neq \begin{cases} \mu(\pi) \\ \text{and} \\ \mu(n) \end{cases}} n_\nu \gamma_{\mu(n)\nu} \qquad (2)$$

The one-center two-electron integrals, $\gamma_{\mu(n)\mu(n)}$, $\gamma_{\mu(\pi)\mu(n)}$, and $K_{\mu(\pi)\mu(n)}$ (exchange integral), have been obtained from atomic spectral data.

In the calculation of $\gamma_{\mu(n)\nu(n)}$ and $\gamma_{\mu(\pi)\nu(n)}$, where μ and ν are nonneighbours, the orbital $\mu(n)$ has been replaced by a uniformly charged sphere with its origin in the centre of charge of the chosen localized hybrid orbital.

The parameters to be determined are:

$W_{N(n)}$ where the nitrogen atom has two carbon neighbours;

$\Delta W_{N_1(n)}$ (N_2) is the correction due to the replacement of a carbon atom by a nitrogen atom;

$\beta_{N_1(n)N_2(n)}$ $(ortho)$, $\beta_{N_1(n)N_3(n)}$ $(meta)$, and $\beta_{N_1(n)N_4(n)}$ $(para)$;

$\gamma_{N(n)C(\pi)}$ where N and C are neighbours; and

$\left.\begin{array}{l}\gamma_{N_1(n)N_2(\pi)} \\ \gamma_{N_1(n)N_2(n)}\end{array}\right\}$ where N_1 and N_2 are neighbours.

In order to limit the number of parameters, no distance dependence has been introduced. Furthermore, the following approximation was made:

$$\gamma_{N_1(n)N_2(n)} = \gamma_{N_1(n)N_2(\pi)} = \gamma_{N_1(\pi)N_2(\pi)} \tag{3}$$

The remaining six parameters have been determined through a least squares fit to the following experimental data: the lone pair ionization potential of pyridine; the second lone pair ionization potential of pyrimidine, pyrazine and pyridazine. The lowest $n - \pi^*$ singlet transitions [18] of pyridine, pyrimidine, and pyridazine were also taken into account.

Turner's (1966) photoelectron-spectroscopy data [17] were used, as they give accurate IP values for a whole series of standard molecules. These data correspond to adiabatic IP values. In the future, when more high-resolution spectra are available, it will be easy to modify the present parameter sets, using experimental vertical IP values. Preliminary calculations on diazabenzenes showed that the lowest IP (n) and the second IP (π) were to be found in the same region around 10 eV. The observed IP value around 11 eV was assigned as the second IP (n), as previous calculations on the π-system gave no IP (π)-values in that region. These second IP (n) values for pyrimidine, pyrazine, and pyridazine were thus chosen for parameter determination.

To obtain an electrically allowed $n - \pi^*$ singlet transition of symmetry $^1B_{3u}$ in the region $30 - 34$ kK for pyrazine,[19] it was necessary to choose a positive value of $\beta_{N(n)N'(n)}$ $(para)$. As it may still be a question whether also an electronically forbidden singlet $n - \pi^*$ transition $(^1B_{2g})$ is located in that region,[20,21] an explicit experimental value of the $^1B_{3u}$ transition for pyrazine was not used for the parameter determination. In this context it is interesting to note that the final results show just one $n - \pi^*$ singlet, $^1B_{3u}$, in this region. The forbidden $n - \pi^*$ transition, $^1B_{2g}$, is found in the same region as the first $\pi - \pi^*$ singlet transition (cf. Table 4 and Ref. 3).

The obtained parameters are found in Table 1. The method can easily be extended to other heteroatomic molecules containing lone pairs.

III. RESULTS AND DISCUSSION

The parameter values, listed in Table 1, were used in a study of the electronic structure and the electronic spectra of a series of molecules containing nitrogen atoms. The numbering of atoms and choice of axes are given in Fig. 1.

Table 1. Semi-empirical parameters for σ lone pair, n, in nitrogen containing molecules. Two sets of parameters are given. In the determination of one-center and non-neighbour two-electron integrals, the lone pair orbital has been considered as a localized orbital with I, sp^2 hybridization; and II, 10 % s character. All values in eV. For notations, see text.

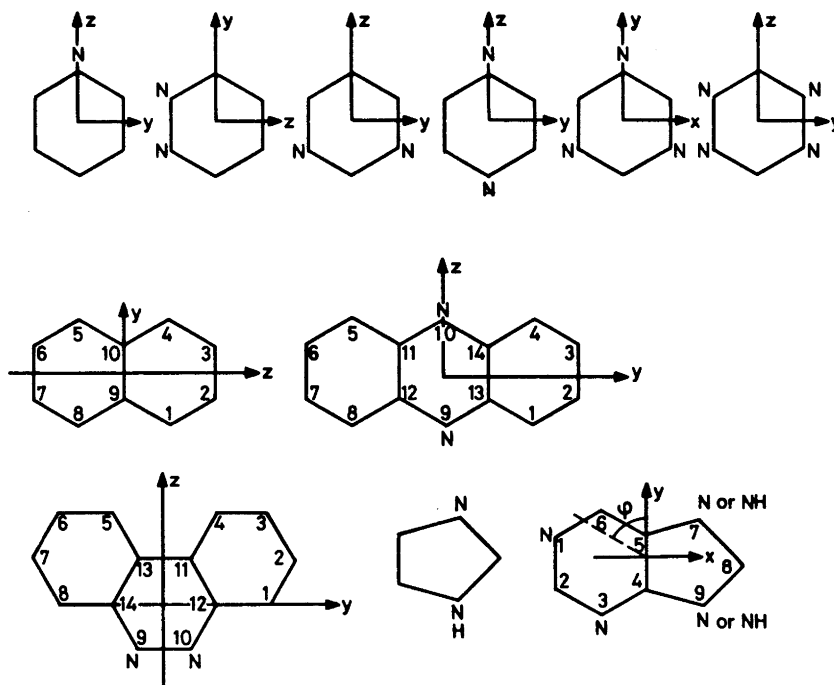| n Parameters	I	II
$\gamma_{N_1(n)N_1(n)}$	17.53	16.32
$\gamma_{N_1(n)N_1(\pi)}$	13.95	13.83
$K_{N_1(n)N_1(\pi)}$	1.57	1.05
$\gamma_{N_1(n)C_2(\pi)}$	7.36	6.28
$\gamma_{N_1(n)N_2(\pi)}$	9.00	9.00
$\gamma_{N_1(n)N_2(n)}$	9.00	9.00
$\beta_{N_1(n)N_2(n)}$ (*ortho*)	-0.563	-0.395
$\beta_{N_1(n)N_3(n)}$ (*meta*)	-0.620	-0.607
$\beta_{N_1(n)N_4(n)}$ (*para*)	$+0.569$	$+0.528$
$W_{N(n)}$	-10.90	-11.02
$\Delta W_{N_1(n)}(N_2)$	-0.19	-0.30

Fig. 1. Symmetry axes and notations of atoms.

The results obtained are collected in Tables 2 − 17, together with available experimental data.

1. Bond lengths. A suitable geometry (experimentally determined when available, otherwise assumed) for the molecules was chosen to start with. Bond distances were obtained from the calculated bond orders, $p_{\mu\nu}$ by means of the relations:[1,3,10]

$$R_{\mu\nu} \;(C,C) = 1.517 - 0.18 \; p_{\mu\nu} \qquad (4)$$

$$R_{\mu\nu} \;(C,N) = 1.458 - 0.18 \; p_{\mu\nu} \qquad (5)$$

$$R_{\mu\nu} \;(N,N) = 1.453 - 0.18 \; p_{\mu\nu} \qquad (6)$$

For those molecules where the bond distances, $R_{\mu\nu}$, deviated by more than ± 0.01 Å from the input value for any bond, the calculation was repeated with the obtained values as input for the new geometry. This procedure was repeated until selfconsistency was achieved.

Calculated values of bond lengths for azabenzenes, imidazole, and purines have been published previously.[3,22] For the rest of the molecules here treated, the calculated bond lengths are given in Table 2. These results are very close to previous theoretical determinations by Tinland.[23]

Table 2. Calculated and experimental (for phenazine only) bond lengths in Å. The numbering of the atoms is given in Fig. 1.

Bond	Phthalazine calc.	Cinnoline calc.	Quinazoline calc.	Quinoxaline calc.	1,5-Naphthpyridine calc.
1 − 2	1.325	1.315	1.323	1.321	1.321
2 − 3	1.347	1.358	1.357	1.419	1.420
3 − 4	1.325	1.381	1.321	1.321	1.377
5 − 6	1.379	1.378	1.379	1.378	1.321
6 − 7	1.416	1.418	1.417	1.418	1.420
7 − 8	1.379	1.378	1.378	1.378	1.377
1 − 9	1.423	1.364	1.360	1.359	1.362
8 − 9	1.424	1.426	1.426	1.427	1.425
4 − 10	1.423	1.421	1.423	1.359	1.425
5 − 10	1.424	1.426	1.424	1.427	1.362
9 − 10	1.414	1.414	1.416	1.417	1.416

Bond	Phenazine calc.	Phenazine exp.[66]	Bond	9,10-Diazaphenanthrene calc.
1 − 2	1.369	1.375[a]	1 − 2	1.386
2 − 8	1.430	1.412	2 − 3	1.408
5 − 11	1.430	1.408[a]	3 − 4	1.387
10 − 11	1.342	1.345[a]	9 − 10	1.303
11 − 12	1.428	1.433	4 − 11	1.414
			1 − 12	1.415
			10 − 12	1.379
			11 − 12	1.410
			11 − 13	1.443

[a] The arithmetic mean of the values published by Herbstein and Schmidt.[66]

2. Ionization potentials. The predicted molecular vertical ionization potentials, estimated by Koopman's theorem, are given in Tables 3 and 4. Previous calculations of IP (π)-values [3],[24] by the present method have shown a very good agreement between calculated and observed values not only for the first ionization potential but also for higher ionization potentials. For some of the molecules here treated, several different assignments, based on experiments [17],[25],[26] as well as on MO calculations,[14],[27–30] have been made. Especially the question of the nature of the first IP has been widely dis-

Table 3. Calculated and observed ionization potentials. Values in eV. Previously published IP(π)-values [3],[10] are quoted to allow comparison with experimental data.

Molecule	Ref.	IP					
Pyridine	Obs.[26]	9.31	(9.51)	10.45	12.30		(13.83)
	Obs.[17]	9.28*	*b*	10.54*	12.22		13.83
	Calc. I	9.27	9.72	10.46	—	12.78	—
	Calc. II	»	»	10.51	—	»	—
	Sym.[a]	$a_2(\pi)$	$b_1(\pi)$	$a_1(n)$	$b_2(\sigma)^c$	$b_1(\pi)$	?
Pyridazine	Obs.[26]	8.90	(9.22)	10.53	11.16		13.63
	Obs.[17]	8.91		10.55	11.13*		13.59*
	Calc. I	9.62	9.99	10.26	11.12		13.59
	Calc. II	»	10.34	»	11.13		»
	Sym.[a]	$a_2(\pi)$	$b_2(n)$	$b_1(\pi)$	$a_1(n)$		$b_1(\pi)$
Pyrimidine	Obs.[26]	9.42	(9.64)	10.39	11.06		13.62
	Obs.[17]	9.47*		10.39	11.11*		13.60
	Calc. I	9.50	9.91	10.06	11.15		13.15
	Calc. II	»	9.92	»	11.13		»
	Sym.[a]	$b_1(\pi)$	$b_2(n)$	$a_2(\pi)$	$a_1(n)$		$b_1(\pi)$
Pyrazine	Obs.[35]	9.62		10.16	11.38	11.83	13.60
	Obs.[26]	9.36	(9.51)	10.15	11.14	11.73	13.13
	Obs.[17]	9.27*		10.11	11.15*	11.68	13.10
	Calc. I	9.32	10.01	10.30	11.15	—	13.13
	Calc. II	»	10.10	»	»	—	»
	Sym.[a]	$b_{1g}(\pi)$	$a_g(n)$	$b_{2g}(\pi)$	$b_{1u}(n)$	$b_{3g}(\sigma)^d$	$b_{3u}(\pi)$

[a] Symmetry axes labelled according to Mulliken's conventions [39] (see also Fig. 1).

* Data used for parameter determination.

b According to Baker [25] there are two bands in the lowest energy region (*cf.* text).

c Assignment made by Lindholm [34] (*cf.* text).

d In an *ab initio* SCF calculation, Petke *et al.*[38] obtained the same order of orbital energies as in the present investigation. In between $b_{1u}(n)$ and $b_{3u}(\pi)$ they obtained a $b_{3g}(\sigma)$ orbital (*cf.* text).

Table 4. Calculated and observed ionization potentials. Values given in eV. Symmetry axes, see Fig. 1.

Molecule		IP									
sym-Triazine	Calc. I	9.97	10.08	11.83	13.48						
	Calc. II	9.93	10.08	11.74	13.48						
	Sym.	$e'(n)$	$e''(\pi)$	$a_1'(n)$	$a_2''(\pi)$						
sym-Tetrazine	Calc. I	9.06	9.96	11.32	11.42	11.43	11.69		14.33		
	Calc. II	9.42	9.96	11.26	11.42	11.42	11.44		14.33		
	Sym.	$b_{3g}(n)$	$b_{2g}(\pi)$	$b_{2u}(n)$	$b_{1g}(\pi)$	$a_g(n)$	$b_{1u}(n)$		$b_{3u}(\pi)$		
Phthalazine	Obs.[26]	8.68	9.17	9.68	10.77		12.07	(12.58)	14.09	15.23	
	Calc. I	8.37	9.21	9.78	10.28	10.91	11.96		13.51		
	Calc. II	8.37	9.21	10.16	10.28	10.95	11.96		13.51		
	Sym.	$a_2(\pi)$	$b_1(\pi)$	$b_2(n)$	$a_2(\pi)$	$a_1(n)$	$b_1(\pi)$		$b_1(\pi)$		
Cinnoline	Obs.[26]	8.51	9.03	9.75	10.83		12.04	(12.46)	13.85	16.16	
	Calc. I	8.52	9.08	9.97	10.49	11.10	11.89		13.74		
	Calc. II	8.52	9.08	10.35	10.49	11.14	11.89		13.74		
	Sym.	π	π	n	π	n	π		π		
Quinazoline	Obs.[26]	—	9.02	9.74	10.72	11.26	12.02		13.78	(14.41)	16.28
	Calc. I	8.37	8.99	9.87	10.51	11.12	11.61		13.33		
	Calc. II	8.37	8.99	9.84	10.51	11.10	11.61		13.33		
	Sym.	π	π	n	π	n	π		π		
Quinoxaline	Obs.[26]	—	8.99	—	10.72	—	11.58	(12.32)	13.98	15.30	16.21
	Calc. I	8.44	8.80	9.97	10.79	11.11	11.45		13.40		
	Calc. II	8.44	8.80	9.85	10.79	11.08	11.45		13.40		
	Sym.	$a_2(\pi)$	$b_1(\pi)$	$a_1(n)$	$a_2(\pi)$	$b_2(n)$	$b_1(\pi)$		$b_1(\pi)$		
1,5-Naphthpyridine	Calc. I	8.37	8.63	10.39	10.41	10.41	11.39		13.17		
	Calc. II	8.37	8.63	10.39	10.40	10.40	11.39		13.17		
	Sym.	π	π	π	n	n	π		π		
Phenazine	Obs.[21]	8.4			9.9						
	Calc. I	7.80	8.64	9.19	9.84	10.63	10.92	10.98	12.03	13.38	
	Calc. II	7.80	8.64	9.19	9.88	10.63	10.92	10.94	12.03	13.38	
	Sym.	$b_{2g}(\pi)$	$b_{1g}(\pi)$	$a_u(\pi)$	$a_g(n)$	$b_{3u}(\pi)$	$b_{2g}(\pi)$	$b_{1u}(n)$	$b_{1g}(\pi)$	$b_{3u}(\pi)$	
9,10-Diazaphenanthrene	Calc. I	8.356	8.362	9.61	9.99	10.53	11.32	11.88	12.14	13.90	
	Calc. II	8.356	8.362	9.61	9.99	10.14	11.27	11.88	12.14	13.90	
	Sym.	$a_2(\pi)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	$b_2(n)$	$a_1(n)$	$b_1(\pi)$	$a_2(\pi)$	$b_1(\pi)$	
Imidazole	Calc. I	8.36	9.49	9.52	12.57						
	Calc. II	8.36	9.49	9.82	12.57						
	Sym.	π	π	n	π						
9H-Purine	Calc. I	8.15	8.63	9.51	9.86	10.42	10.78	11.72	13.36		
	Calc. II	8.15	8.63	9.52	10.06	10.42	10.77	11.72	13.36		
	Sym.	π	π	n	n	π	n	π	π		
7H-Purine	Calc. I	8.34	8.50	9.41	9.83	10.46	10.66	11.72	13.37		
	Calc. II	8.34	8.50	9.52	10.01	10.46	10.74	11.72	13.37		
	Sym.	π	π	n	n	π	n	π	π		

cussed.[31-33] Identification of ionization processes as π, σ, or n ionizations has until now been made with confidence for only a few number of ionization processes of these molecules.

Turner, in 1966,[17] published photoelectron spectroscopy (PS) data of azabenzenes. Later, Turner [82] and Baker [25] reported high resolution PS data for some of these molecules. Dewar and Worley [26] recently have given PS results for azabenzenes and azanaphthalenes.

In the following, the calculated IP-values for some of the molecules will be discussed in detail in comparison with experimental values and other MO results.

Pyridine. From an analysis of the vibrational fine structure of the high resolution PS bands, Baker [25] makes the conclusions that the first band is composed of two separate components attributable to two π orbitals, and that the second band at around 10.5 eV is an n level. This is in accordance with the calculated values and order of orbital energies of the present investigation (*cf.* Table 3), and also in agreement with *ab initio* SCF MO results by Clementi [27] and Petke *et al.*,[28] who both obtained the order 1 $a_2(\pi)$, 2 $b_1(\pi)$, 11 $a_1(n)$, 7 $b_2(\sigma)$, 1 $b_1(\pi) \cdots$. Their orbitals 7 $b_2(\sigma)$ and 1 $b_1(\pi)$ are close in energy, indicating that the observed third band starting at 12.2 eV may be composed of two bands. Apart from the lowest IP, Dewar and Worley [26] give a different assignment based on an all valence MO method, MINDO. They obtain the order IP$_1$ (π), IP$_2$ (n) in the lowest energy region, and IP$_3$ (π), IP$_4$ (σ) in the region 10−11 eV. Recently, Johnsson *et al.*[34] have thoroughly analysed ionization processes in pyridine by investigating PS data, Rydberg transitions, and mass spectral measurements. They conclude that the band starting at 12.2 eV corresponds to a bonding σ orbital.

Pyrazine. Eland [35] has recently published high resolution PS data for pyrazine, giving values of vertical ionization potentials. Like Baker, and Dewar and Worley, he concludes that the first ionization is from a π orbital. A comparison between different MO calculations of pyrazine has previously been published by the present author.[24] The calculated order of orbital energies (*cf.* Table 3) is in agreement with del Bene and Jaffe's [30] CNDO-results, and the *ab initio* SCF results of Petke *et al.*[28] The *ab initio* SCF studies by Clementi [27] and Petke *et al.*[28] show that the orbital energies of $1b_{1g}(\pi)$ and $6a_g(n)$ are very close. Clementi's results even give a reversed order of these orbitals, like the all valence calculations by Yonezawa *et al.*[29] Dewar has also suggested two close bands in the lowest energy region, while Eland's data and the present calculations show only *one* band in the lowest energy region.

According to the present investigation, the lowest IP(n) and IP(π_2) are to be found in the same energy region, indicating that the observed band at around 10 eV may be composed of two bands.

Pyrimidine. The present investigation gives the same order of orbital energies as for pyrazine (Table 3). The lowest IP(n) and IP(π_2) are also here found in the same energy region around 10 eV. Del Bene and Jaffé obtained the same order from their CNDO calculation, while Yonezawa *et al.* predict an n orbital to be the highest occupied orbital. Baker makes the interpretation of his PS-data that the first ionization is from a π level, an assignment also made by Yencha and El-Sayed [32] from an analysis of their photoionization

measurements. Dewar, on the contrary, attributes the first IP to an n ionization. This controversy can finally be solved by a careful analysis of high resolution PS data in combination with a study of other types of experiments (*cf.* the analysis of benzene [36] and pyridine [34] by Lindholm and co-workers).

Table 5. Calculated and observed $n-\pi^*$ singlet transitions of azabenzenes. Calculated $\pi-\pi^*$ transitions have been published previously.[3,10] The $\pi-\pi^*$ singlet transitions of *sym*-triazine are given, as there unfortunately was an error in previously published data.[3] Transition frequencies in kK.

Molecule	Calculations			Observations			
				Ref. 18	Ref. 40		
	Sym.[a]	$\nu(\text{I})$	$\nu(\text{II})$	ν_{max}	$\nu(0-0)$	f	Sym.[a]
Pyridine	$^1B_1(A)$	36.6	36.7	*37.0	34.771	0.003	$^1B_1$
	$^1A_2(F)$	48.8	52.6				
	$^1B_1(A)$	77.7	77.7				
Pyrimidine	$^1B_1(A)$	34.0	33.8	*33.5	31.073	0.007	$^1B_1$
	$^1A_2(F)$	36.5	36.7				$^1A_2(?)$
	$^1A_2(F)$	47.4	50.8				
	$^1B_1(A)$	52.4	55.0		51.14	~ 0.005	$^1B_1(?)$
	$^1A_2(F)$	75.3	74.8				
	$^1B_1(A)$	82.7	82.5				
Pyrazine					~ 30.425		
	$^1B_{3u}(A)$	33.3	33.6	30.5	30.876	0.010	$^1B_{3u}$
	$^1B_{2g}(F)$	39.4	39.7				
	$^1A_u(F)$	44.7	48.9				
	$^1B_{1g}(F)$	53.9	57.4		54(?)		$^1B_{3u}(?)$
	$^1B_{2g}(F)$	77.3	77.1				
	$^1B_{3u}(A)$	83.3	83.2				
Pyridazine	$^1B_1(A)$	29.4	29.4	*29.4	26.649	0.006	$^1B_1$
	$^1A_2(F)$	36.2	35.1				
	$^1A_2(F)$	43.4	46.7				
	$^1B_1(A)$	49.7	52.2		$\begin{cases} 50.865 \text{ or} \\ 51.503 \end{cases}$	—	$^1B_1(?)$
	$^1B_1(A)$	72.3	74.0				
	$^1A_2(F)$	80.8	80.2				
sym-Triazine	$^1A_2''(A)$	33.4	32.3	36.8	31.574	~ 0.018	$^1A_2''$
	$^1E''(F)$	35.0	35.0		32.500	—	$^1A_1'', {}^1E''$
	$^1A_1''(F)$	43.6	47.4				
	$^1A_2'(F)\pi-\pi^*$	44.0			44.000	~ 0.002	$^1A_2'$
	$^1E''(F)$	53.5	56.3				
					55.782		$^1A_2''$ or $^1E'$
	$^1A_1'(F)\pi-\pi^*$	59.6					
	$^1E'(A)\pi-\pi^*$	62.3					
	$^1E''(F)$	76.4	75.4				
	$^1E'(A)\pi-\pi^*$	77.0					
	$^1E'(A)\pi-\pi^*$	82.1					
	$^1A_2''(A)$	87.9	87.2				

Table 5. Continued.

	$^1B_{3u}(A)$	22.1	21.9	18.6	18.129	0.0042	$^1B_{3u}$
	$^1A_u(F)$	30.6	32.9				
				~31.25		~0.001	$^1B_{3u}$, ^1A_u
	$^1B_{1g}(F)$	33.8	33.6				or $^1B_{2g}$
sym-	$^1B_{2g}(F)$	37.7	34.6				
Tetrazine	$^1A_u(F)$	40.7	40.3				
	$^1B_{3u}(A)$	50.9	52.7				
	$^1B_{1g}(F)$	51.1	53.3				
	$^1B_{2g}(F)$	51.8	55.8				
	$^1B_{1g}(F)$	70.8	72.2				
	$^1B_{3u}(A)$	83.5	84.6				
	$^1A_u(F)$	84.3	83.2				
	$^1B_{2g}(F)$	85.2	84.2				

[a] Symmetry axes labelled according to Mulliken's conventions.[39]
A. Allowed (electronically).
F. Forbidden (electronically).
* Data used for parameter determination.

Pyridazine. Gropen and Skancke [10] have previously discussed assignments of the measured ionization potentials of pyridazine. Pyridazine has also been discussed by Yencha and El-Sayed,[32] and commented by Del Bene and Jaffé.[33] Like the CNDO-calculations of Del Bene and Jaffé, the present results show that the lowest ionization is from a π orbital, a tentative assignment also made by Baker from his PS data. Dewar attributes IP_3 to an n ionization, and so do Yonezawa *et al.*

sym-*Triazine and* sym-*tetrazine.* Here, the present calculations give the result (Table 4) that the lowest ionization is from an n orbital. As far as is known to the author, there are no accurate IP measurements of these molecules. It will of course be very interesting to see whether future high resolution PS measurements do confirm the predictions made by the present method.

Azanaphthalenes. In Table 4, the calculated values are given together with Dewar's PS data for azanaphthalenes. It is interesting to note the good agreement, especially for phthalazine and cinnoline, for which molecules Dewar has suggested a different assignment.

Purines. There are no accurate IP measurements for these molecules. Pullman and Rossi [37] have suggested that $IP(\pi) < IP(n)$ for all biochemical purines, in accordance with the present results.

3. Electronic spectra. The electronic transition energies have been calculated by configurational mixing of all singly excited configurations. The oscillator strengths have been estimated from the standard formula of Mulliken and Rieke.[38]

In Tables 5 – 14, the calculated singlets are collected and compared with available experimental data. The lowest n-π^* and π-π^* triplets are given in Tables 15 – 17. The parameter scheme used in the present investigation and in other papers of this series [1-10] is adopted to give agreement between calculated and observed singlet transitions of a chosen set of small standard molecules. The parametrization implicitly takes account of part of the correlation. Since

Table 6. Electronic singlet transitions of phthalazine. Transition frequencies in kK.

Calculations				Observations								
Sym.	(I)	(II)	f	Marzacco,[48] crystal spectra				Hirt et al.,[67] in cyclohexane			Müller and Dörr,[68] in heptane	
				Sym.	Range	ν_{0-0}	ε_{max}	Range	ν_{max}	ε_{max}	Sym.	ν_{0-0}
$^1B^1(A)$ $n\!-\!\pi^*$	31.7	32.6		$^1A_2$	25—27	25.259		25—30	27.5[s]	41	$n\!-\!\pi^*$	25.820
$^1A_2(F)$ $\pi\!-\!\pi^*$	33.3	35.9	0	$^1A_2$	27—29	27.016[a]	788	32—36	34.48	870	^1L_b	33.000
$^1A_1(z)$ $\pi\!-\!\pi^*$	34.8		0.01	$^1A_1$		32.79		37—40	38.6	4100	^1L_a	37.430
$^1B_2(y)$ »	40.3		0.25	$^1B_2$		35.76	3800					
$^1A_2(F)$ $n\!-\!\pi^*$	44.9	44.8	0									
$^1B_1(A)$ » »	46.1	48.0	0.0003									
$^1A_1(z)$ $\pi\!-\!\pi^*$	48.4		0.0014									
$^1B_2(y)$ »	48.7		1.97					43—	47.1	59500	^1B_b	46.500
$^1A_1(z)$ »	51.5		0.0003									
$^1B_2(y)$ »	52.7		0.78									
$^1B_2(y)$ »	54.4		0.0032									
$^1A_1(z)$ »	62.3											

[s] Shoulder.
[a] Origin assumed, not observed.

Table 7. Electronic singlet transitions of cinnoline. Transition frequencies in kK.

	Calculations				Observations			
					Wait and Grogan,[69] vapour		Favini and Bellbono,[70] in hexane	
Sym.	ν(I)	ν(II)		f	Sym.	ν_{0-0}	ν_{max}	$\dfrac{f}{2\times10^{-5}\varepsilon_{max}}$
$n-\pi^*$	26.3	26.2			$n-\pi^*$	22.711		
$\pi-\pi^*$		34.9		0.03	$\pi-\pi^*$	31.542	32.2	0.03
$n-\pi^*$	35.1	32.5						
$\pi-\pi^*$		40.8		0.19			37.5	0.095
$n-\pi^*$	45.5	50.3						
$\pi-\pi^*$		48.4		0.15			45.6	0.86
»		50.5		0.40				
»		51.2		1.48			50.7	0.84
»		53.6		0.26				
$n-\pi^*$	54.1	56.7						
»	61.0	63.5						
$\pi-\pi^*$		61.5		0.03				

correlation effects are different for singlet and triplet states, the present parameters will give too low values for triplets. The singlet-triplet splitting is around 1 eV too large consistent with the value of the pair correlation energy.

Table 8. Electronic singlet transitions of quinazoline. Transition frequencies in kK.

	Calculations				Observations			
					Favini and Bellobono,[70] in hexane		Hasegawa et al.,[71] vapour	
Sym.	ν(I)	ν(II)		f	ν_{max}	$\dfrac{f}{2\times10^{-5}\varepsilon_{max}}$	Sym.	ν_{0-0}
$n-\pi^*$	31.8	31.6					$n-\pi^*$	27.581
$\pi-\pi^*$		34.7		0.03	32.2	0.03		
$n-\pi^*$	36.3	36.6						
$\pi-\pi^*$		40.9		0.21	37.5	0.095		
»		48.5		0.21	45.7	0.86		
$n-\pi^*$	48.6	51.6						
$\pi-\pi^*$		50.3		1.15	50.7	0.84		
»		52.6		0.49				
»		53.8		0.51				
»		54.3		0.49				
$n-\pi^*$	54.5	57.7						
»	60.9	60.9						
$\pi-\pi^*$		61.9		0.048				

Table 9. Electronic singlet transitions of quinoxaline. Transition frequencies in kK.

| | Calculations | | | Observations | | | | | | | | |
| | | | | Marzacco,[43] crystal spectra | | | Hasegawa et al.,[72] vapour | | Kummer and Zimmermann,[73] in heptane | | Favini and Bellobono,[70] in hexane | |
Sym.	(I)	(II)	f	Sym.	range	ν_{0-0}	Sym.	ν_{0-0}	Sym.	ν_{0-0}	ν_{max}	f $2\times10^{-5}\varepsilon_{max}$
$^1B_1(A)$ $n-\pi^*$	30.7	30.5	0.05	$^1B_1$	25.8–28.6	25.825	$n-\pi^*$	26.017	$n-\pi^*$	26.6		
$^1A_1$ $\pi-\pi^*$	34.3			$^1A_1$		30.8			^1L_b	31.5	31.5	0.065
$^1A_2(F)$ $n-\pi^*$	36.8	36.8										
$^1B_2$ $\pi-\pi^*$	40.8		0.14									
$^1A_1$ »	48.2		0.56						^1L_a	~34	34.3^s	0.085
$^1A_2(F)$ $n-\pi^*$	49.0	52.0	0									
$^1A_1$ $\pi-\pi^*$	51.6		1.47						^1B_b	42.3	43.1	0.33
$^1B_2$ »	51.8		0.64									
$^1B_2$ »	54.1		0.005									
$^1B_2$ »	56.3		0.25									
$^1B_1(A)$ $n-\pi^*$	56.4	59.7									51.0	0.69
$^1B_1(A)$ »	60.4	60.6										
$^1A_1$ $\pi-\pi^*$	61.4		0.03									

Table 10. Electronic singlet transitions of 1,5-naphthpyridine. Transition frequencies in kK.

Calculations				Observations				
				Favini et al.,[74] in cyclohexane		Müller and Dörr,[68] in heptane		
Sym.	ν(I)	ν(II)	f	ν	f	ν_{max}	Range	log ε
$\pi-\pi^*$		34.2	0.06	32.5	0.13	34	31 – 38	3.5
$n-\pi^*$	34.6	34.4						
$\pi-\pi^*$		42.1	0.12	38.9	0.094	42	37 – 45	3.7
»		48.2	0					
»		50.8	2.07	48.5	1.08			
»		52.1	0.91					
»		52.8	0					
$n-\pi^*$	53.1	56.1						
$\pi-\pi^*$		55.0	0					
»		61.1	0					
»		62.5	0					
$n-\pi^*$	62.8	63.3						
$\pi-\pi^*$		64.4	0					

According to the preceding discussion it is not possible to obtain good agreement with experimental spectral data for both singlets and triplets with the same set of parameters. When more accurate triplet spectral data are available, it will be possible to determine in the same way parameters to be used for calculations of triplet state energies. The calculated relative order of the triplets is expected to be given correctly by the present method. As far as is known to the author, no triplet-triplet absorption data are found in the literature for the molecules treated here. The results of the present investigation can give an indication of where triplet-triplet transitions are to be found.

As $\pi-\pi^*$ transitions calculated by the present method have been thoroughly discussed in previous paper,[3,22] the following discussion will be concentrated on $n-\pi^*$ transitions.

Azabenzenes. Calculated and observed singlet $n-\pi^*$ transitions of azabenzenes are given in Table 5. Symmetry axes are labelled according to Mulliken's conventions.[39,40] $\pi-\pi^*$ singlet transitions calculated by the present method have been published previously.[3,10] The overall agreement with experimental findings is satisfactory, especially for calculation I (sp^2 hybridization assumed).

Experimental data and assignments based on orbital considerations have been collected and critically discussed in a review by Innes et al.[40] The spectral data tabulated in their article will be used for comparison with calculated values throughout this paragraph. Hochstrasser et al. have recently published low-temperature electronic absorption spectra of several aromatic azines.[41-46] They have thoroughly discussed the nature of the lowest $n-\pi^*$ and $\pi-\pi^*$ triplet and singlet states and the perturbations between these states. In the literature, there have been some discussions about the nature of the lowest

Table 11. Electronic singlet transitions of phenazine. Transition frequencies in kK.

| | Calculations | | | Observations | | | | | | | |
| | | | | Hochstrasser,[75] crystal spectra | | Kummer and Zimmermann,[73] in ethanol | | | Perkampus and Kortüm [76] | | |
Sym.[a]	ν(I)	ν(II)	f	Sym.	ν_{0-0}	Sym.	ν_{0-0}	log ε	Sym.	ν_{0-0}	log ε
$^1B_{3u}(A)$ $n-\pi^*$	29.7	29.0	0.18	$^1B_{3u}$	22.881	^1L_a	25.0	3.5	^1L_a	26.0^s	3.3
$^1B_{1u}(z)$ $\pi-\pi^*$		34.3	0.08			^1L_b	27.3	4.2	^1L_b	27.6	4.1
$^1B_{2u}(y)$ »		30.9	0								
$^1B_{2g}(F)$ $n-\pi^*$	36.3	35.4	0								
$^1B_{3g}(F)$ $\pi-\pi^*$		38.9	1.67			^1B_b	39.6	5.1			
$^1A_g(F)$ »		42.6	0								
$^1B_{3u}(y)$ »		44.0	0.01								
$^1B_{3g}(F)$ »		44.6	0.12								
$^1B_{1u}(z)$ »		48.7									
$^1B_{1u}(z)$ »		50.1									
$^1A_u(F)$ $n-\pi^*$	50.4	53.8	0.30			^1C_b	48.1	4.3			
$^1B_{2u}(y)$ $\pi-\pi^*$		51.1	0.66								
$^1B_{1u}(z)$ »		51.9									
$^1B_{1g}(F)$ $n-\pi^*$	53.8	55.5	0								
$^1A_g(F)$ $\pi-\pi^*$		55.6	0.29								
$^1B_{2u}(y)$ »		56.0	0								
$^1A_g(F)$ »		57.2									
$^1B_{3u}(A)$ $n-\pi^*$	58.4	59.2	0								
$^1B_{3g}(F)$ $\pi-\pi^*$		58.5	0								
$^1A_g(F)$ »		59.4	0.10								
$^1B_{2u}(y)$ »		60.9									

[a] For choice of symmetry axes, see Fig. 1.

Table 12. Electronic singlet transitions of 9,10-diazaphenanthrene. Transition frequencies in kK.

Calculations				Observations					
				Marzacco,[48] crystal spectra			Badger and Walker,[77] in cyclohexane		
Sym.[a]	$\nu(I)$	$\nu(II)$	f	Sym.	Range	ν_{0-0}	ν_{max}	Range	$\log \varepsilon_{max}$
$^1B_1(A)$ $n-\pi^*$	24.6	24.5		$^1B_1$	23−25	23.094	24.4		2.5
$^1A_2(F)$ »	33.6	30.8	0						
$^1A_1(z)$ $\pi-\pi^*$		32.5	0.02					27−31	3.1
$^1B_2(y)$ »		39.0	0.27					32−36	3.7
$^1B_2(y)$ »		39.8	0.004						
$^1B_2(y)$ »		44.8	1,79				~40	36−	4.5
$^1A_1(z)$ »		46.0	0.30						
$^1A_1(z)$ »		48.3	0.39						
$^1B_2(y)$ »		49.8	0.32						
$^1A_1(z)$ »		50.9	0.23						
$^1A_2(F)$ $n-\pi^*$	51.9	56.3	0.						
$^1B_2(y)$ $\pi-\pi^*$		54.1	0.22						
$^1A_1(z)$ »		54.5	0.07						
$^1B_2(y)$ »		57.2	0.02						
$^1B_1(A)$ $n-\pi^*$	58.4	62.2							
$^1A_1(z)$ $\pi-\pi^*$		58.8	0.43						

[a] For choice of symmetry axes, see Fig. 1.

singlet transition in the diazabenzenes (see, *e.g.*, Ref. 47, p. 90). El-Sayed and Robinson,[20,48] from measurements of the absorption spectra in pure crystal at 4°K, concluded that the lowest singlet state was a forbidden $n-\pi^*$ state in all diazabenzenes. Cohen and Goodman [21] based their discussion of radiationless paths in the diazines on this interpretation. Now El-Sayed in a recent publication [49] has stated that the lowest singlet in pyrazine is the allowed $_1B_{3u}(n-\pi^*)$ state, as has also been shown by Innes *et al.*[19] In a recent paper,

Table 13. Electronic singlet transitions of imidazole. Transition frequencies in kK.

Calculations				Observations			
				Gelus and Bonnier,[78] in ethanol		Braude,[60] in ethanol	
Sym.	$\nu(I)$	$\nu(II)$	f	ν_{max}	$\log \varepsilon$	ν_{max}	ε_{max}
$n-\pi^*$	37.9	41.7		48.4	3.32	40.0	60
$\pi-\pi^*$		47.6	0.33			>47.6	>5000
»		52.5	0.04				
$n-\pi^*$	52.3	57.0					
$\pi-\pi^*$		61.4					

Table 14. Electronic singlet transitions of 9H-purine and 7H-purine. Transition frequencies in kK.

9H-purine							7H-purine							
Calculations					Observations Clark and Tinoco,[61] in trimethyl phosphate		Calculations					Observation Chen and Clark,[65] crystal spectra,[b]		
Sym.	ν(I)	ν(II)	f	Pol.[a] $\varphi°$	ν_{max} or range	f	Sym.	ν(I)	ν(II)	f	Pol.	Sym.	ν_{max}	φ^{oc}
n–π^*	35.0	35.4		⊥	33–34.5	0.0035	n–π^*	32.0	32.3		⊥	n–π^*	34	⊥
»	35.5	38.2		⊥			»	35.0	37.2		⊥			
≫	37.6	38.5		⊥			≫	36.2	37.8		⊥			
π–π^*	39.4		0.05	102	37.7	0.1	π–π^*	38.8		0.09	48	π–π^*	38	48
—							—					π–π^*	40	⊥ ~90
π–π^*	43.8		0.36	71	41.7	0.05	π–π^*	45.5		0.13	124		44	
n–π^*	50.9	51.3	0.47	147	49.5		»	51.8		0.35	20			
π–π^*	48.3		0.38	⊥	53.2	0.6	≫	52.2		0.87	94			
»	54.9			91			n–π^*	50.3	53.8		⊥	n–π^*	~53	⊥
»	57.1	51.3	0.48	78			»	55.8	59.3		⊥			

[a] For notations, see Fig. 1.
[b] From polarized reflection spectra.
[c] Approx. free-molecule polarization directions deduced by a simple correction for intermolecular interactions.

Table 15. Electronic triplet transitions of azabenzenes. The lowest $n-\pi^*$ and $\pi-\pi^*$ triplets.[a] Transition frequencies in kK.

Molecule	Calculations			Observations			
				Marzacco,[43] crystal spectra		Innes et al.,[40] vapour	
	Sym.	ν(I)	ν(II)	Sym.	ν_{0-0}	Sym.	ν_{0-0}
Pyridine	$^3A_1$ $\pi-\pi^*$		23.0			$^3A_1$	~ 29.7
	$^3B_1$ $n-\pi^*$	25.2	29.3				
	$^3A_1$ $\pi-\pi^*$		33.6				
Pyridazine	$^3B_1$ $n-\pi^*$	18.3	22.1	$^3B_1$		$^3B_1$	~ 24.8
	$^3A_1$ $\pi-\pi^*$		23.2				
	$^3A_2$ $n-\pi^*$	25.0	27.5				
	$^3B_2$ $\pi-\pi^*$		34.1				
Pyrimidine	$^3A_1$ $\pi-\pi^*$		23.1	$\pi-\pi^*$	$\sim 29.8^b$	$^3A_1{}^c$	
	$^3B_1$ $n-\pi^*$	23.3	26.8	$^3B_1$	28.916	$^3B_1$	29.280
	$^3A_2$ »	25.5	29.5				
	$^3B_2$ $\pi-\pi^*$		34.1				
Pyrazine	$^3B_{3u}$ $n-\pi^*$	22.1	26.2	^3B_3u		$^3B_{3u}$	26.820
	$^3B_{1u}$ $\pi-\pi^*$		23.1	$\pi-\pi^*$			
	$^3B_{2g}$ $n-\pi^*$	27.6	31.9				
	$^3B_{1u}$ $\pi-\pi^*$		34.1				
sym-Triazine	$^3A_2''$ $n-\pi^*$	22.6	25.3			$^3E''$, $^3A_2''$	26.400
	$^3A_2'$ $\pi-\pi^*$		23.2				
	$^3E''$ $n-\pi^*$	24.6	28.0				
	$^3E'$ $\pi-\pi^*$		35.5				
sym-Tetrazine	$^3B_{3u}$ $n-\pi^*$	11.8	15.1				
	$^3B_{1g}$ »	21.7	25.5				
	^3A_u »	21.8	25.7				
	$^3B_{1u}$ $\pi-\pi^*$		23.0				

[a] As the parameters used in the calculations are parameters determined from experimental singlet transitions, the calculated triplet energies will be too low (*cf.* text) in comparison with experimental values.

[b] Estimated from the observed broadening of the vibronic bands.

[c] From phosphorescence polarization data.[79]

Innes and co-workers [50] have published vibrational and rotational analysis of the lowest $n-\pi^*$ singlet transition in pyrimidine from high resolution vapour absorption spectra. Their main conclusion is that all strong bands arise from only one electronic transition, to the allowed $n-\pi^*$ state of symmetry $^1B_1$. From all valence calculations, Yonezawa et al.[29] obtain the result that the lowest singlet state in pyridine and diazabenzenes is an allowed $n-\pi^*$ state, as also found in the present investigation. Del Bene and Jaffé [30] likewise found that the lowest singlet was an $n-\pi^*$ state from their CNDO calculations on the same molecules, but they have not given the symmetries in their

Table 16. Electronic triplet transitions. The lowest $n-\pi^*$ and $\pi-\pi^*$ triplets. Transition frequencies in kK.

Molecule	Calculations			Observation	
	Sym.	ν(I)	ν(II)	Marzacco,[43] crystal spectra — Sym.	ν_{0-0}
Phthalazine	$^3B_2\ \pi-\pi^*$	17.0		$^3B_2$	
	$^3B_1\ n-\pi^*$	20.4	25.2		
	$^3A_2$ »	24.1	28.9		
	$^3A_1\ \pi-\pi^*$	25.7			
Cinnoline	$n-\pi^*$	15.7	19.2		
	$\pi-\pi^*$	17.2			
	$n-\pi^*$	24.0	25.3		
	$\pi-\pi^*$	25.9			
Quinazoline	$\pi-\pi^*$	16.9		$\pi-\pi^*$	[a]
	$n-\pi^*$	22.1	25.2		
	»	25.4	29.4		
	$\pi-\pi^*$	25.9			
Quinoxaline	$^3B_2\ \pi-\pi^*$	17.0		$^3B_2$	[a],[b]
	$^3B_1\ n-\pi^*$	20.4	23.8	$^3B_1$	$\sim$24.4[c]
	$^3A_2$ »	26.1	29.8		
	$^3B_2\ \pi-\pi^*$	26.4			
1,5-Naphthpyridine	$\pi-\pi^*$	16.9			
	$n-\pi^*$	24.3	27.7		
	$\pi-\pi^*$	26.2			
	»	27.8			

[a] Lowest triplet.
[b] El-Sayed and Brewer.[30]
[c] A diffuse absorption that commences at around 24.4 kK.

publication. Observations and identifications of higher $n-\pi^*$ transitions are very scarce. For pyridine, pyrazine, and *sym*-triazine, the present investigation predicts a second allowed $n-\pi^*$ transition in the far UV, where they are probably hidden by Rydberg transitions. They may perhaps be revealed by polarization measurements. For pyridine, a forbidden $n-\pi^*$ transition of symmetry $^1A_2$ is found in the region of the second $\pi-\pi^*$ transition $^1A_1$. In pyrimidine, a second allowed $^1B_1$ $n-\pi^*$ transition is obtained in a region where there are experimental evidence for an $n-\pi^*$ transition.[51] For pyrazine, Innes *et al.*[40] give $^1B_{3u}$ as a tentative assignment of a fragmentary system observed around 54 kK. The present investigation obtains an $n-\pi^*$ singlet in that region, but of symmetry $^1B_{1g}$ (forbidden). A second allowed $n-\pi^*$ singlet is obtained around 50 kK for pyridazine ($^1B_1$) and *sym*-tetrazine ($^1B_{3u}$). For pyridazine, this is in accordance with experiments,[40] while the corresponding *sym*-tetrazine band has not yet been observed as far as is known to the present author. The third allowed $n-\pi^*$ singlet transition is predicted to be found in the far UV for both pyridazine and *sym*-tetrazine.

Table 17. Electronic triplet transitions. The lowest $n-\pi^*$ and $\pi-\pi^*$ triplets. Transition frequencies in kK.

Molecule	Calculations			Observation	
				Marzacco,[43] crystal spectra	
	Sym.	ν(I)	ν(II)	Sym.	ν_{0-0}
Phenazine	$^3B_{1u}$ $\pi-\pi^*$		12.6	$^3B_{1u}$	15.3
	$^3B_{3g}$ »		19.6		
	$^3B_{3u}$ $n-\pi^*$	20.1	22.8	$^3B_{3u}$	~20.8
	$^3B_{2u}$ $\pi-\pi^*$		25.5		
9,10-Diazaphenanthrene	$^3B_1$ $n-\pi^*$	14.0	17.4	$^3B_1$	18.6—23.1[a]
	$^3B_2$ $\pi-\pi^*$		16.7	$^3B_2$	18.568[b]
	$^3A_2$ $n-\pi^*$	22.8	23.7		
	$^3A_1$ $\pi-\pi^*$		23.1		
Imidazole	$\pi-\pi^*$		22.8		
	$n-\pi^*$	27.5	35.1		
	$\pi-\pi^*$		33.7		
	»		40.0		
9H-Purine	$\pi-\pi^*$		20.1		25[c]
	$n-\pi^*$	25.4	29.1		
	»	26.3	31.3		
	»	27.2	32.4		
7H-Purine	$\pi-\pi^*$		20.2		
	$n-\pi^*$	21.6	25.5		
	»	25.0	29.8		
	»	25.7	31.6		

[a] A continuous absorption region.
[b] Assigned as the lowest triplet. $E(^3B_1)-E(^3B_2) \sim <1400$ cm^{-1}.
[c] Cohen and Goodman.[81]

A great number of electronically forbidden $n-\pi^*$ singlet transitions are found in the present investigation. Some of the results can be used for assignments of now available experimental data. The $^1B_{2g}$ band of pyrazine has already been mentioned in Section II. In *sym*-triazine, the observed band at 32.500 cm^{-1} can be assigned as a $^1E''$ transition, also suggested by Brinen and Goodman.[51] The intense sharp system observed at 55.782 cm^{-1} for *sym*-triazine has been assigned [40] as $^1A_2''$ (allowed $n-\pi^*$) or $^1E'$ (allowed $\pi-\pi^*$), while the present investigation suggests $^1E''$ (forbidden $n-\pi^*$) or $^1A_1'$ (forbidden $\pi-\pi^*$) as possible assignments. For *sym*-tetrazine, the calculations give as much as four forbidden $n-\pi^*$ transitions in the region 30—40 kK, where experimentally a shoulder of the first $\pi-\pi^*$ singlet band is found.[40]

Yonezawa *et al.*[29] have published the two (for pyrimidine three) lowest $n-\pi^*$ singlets from their all valence calculations. For the diazines, they obtain the same ordering of these levels as found in the present investigation, but their calculated transition energies deviate more from experimental

values. Del Bene and Jaffé [30] have only quoted data for the lowest $n-\pi^*$ singlets from their CNDO calculations.

As shown in Table 15, the obtained relative order (from calculation I) between the lowest $n-\pi^*$ and $\pi-\pi^*$ triplet transitions is in accordance with available experimental data. Pyridine and pyrimidine have $\pi-\pi^*$ states as lowest triplets, while an $n-\pi^*$ state is the lowest triplet for the other molecules studied. In pyrimidine, the $^3A_1$ ($\pi-\pi^*$) and $^3B_1$ ($n-\pi^*$) are found to be very close in energy.

This is one of the cases for which Hochstrasser and Marzacco [45] have suggested that the interpretation of experimental spectroscopic data might be complicated by the possibility of the breakdown of the Born-Oppenheiner approximation.

Azanaphthalenes, phenazine and 9,10-diazaphenanthrene. Calculated singlet transitions are given in Tables 6 − 10. As for azabenzenes, the results of calculation I (sp^2 hybridization) seem to be in somewhat better overall agreement with experimental data than the results of calculation II (10 % s character), although the main pattern for almost all molecules treated is the same for both calculations. In this context, it should be stressed that the present simple method cannot be expected to account for finer details of azine spectra depending on, *e.g.*, large geometrical change between ground and excited states,[52] the breakdown of the Born-Oppenheimer approximation [45] and strong core charge rearrangements in the excited states. Until these effects can be accounted for by a more refined theoretical approach, the present semi-empirical method with all its limitations can be used as a first step in making assignments of the electronic states of nitrogen-containing molecules.

According to calculation I of the present investigation, phthalazine has two $n-\pi^*$ singlet transitions below the first $\pi-\pi^*$ singlet, as was also suggested by Mason [53] from solution spectral data. The lowest $n-\pi^*$ singlet state is predicted to be a weakly allowed state of symmetry $^1B_1$, and the second $n-\pi^*$ state a forbidden state of symmetry $^1A_2$ (Table 6). As can be seen from Tables 4 and 11, $^1B_1$ is also predicted to be the lowest singlet state in the other *ortho*-diazines, belonging to the same symmetry group, namely, pyridazine and 9,10-diazaphenanthrene, where there are experimental verifications that the lowest band is of symmetry $^1B_1$.[40,43] From a vibrational analysis of crystal spectra of phthalazine, Hochstrasser and Marzacco [43,44] also conclude that there are two $n-\pi^*$ singlet states preceding the lowest $\pi-\pi^*$ singlet, but they make the assignment that both are $^1A_2$ states. Their data do not, however, exclude $^1B_1$ as a possible assignment of the lowest band. The two bands overlap considerably, thereby complicating the vibrational analysis.

Calculated triplet states are given in Tables 16 and 17, together with Marzacco's crystal absorption spectral data.[43] Most two- and three-ring azines are expected to have a lowest $\pi-\pi^*$ triplet state (Ref. 47, Chapter 6). The results of the present investigation tend to confirm this rule, the only exceptions being the *ortho*-diazines cinnoline and 9,10-diazaphenanthrene.

For phthalazine, the present investigation predicts the lowest triplet to be a $^3B_2$ ($\pi-\pi^*$) state in accordance with conclusions made by Marzacco [45] from a study of the phosphorescence spectrum in ethanol and acidic ethanol solutions at 77°K. Another assignment has been proposed by Lim and Yu [54]

who assign the lowest triplet to be a $^3n-\pi^*$ state from a comparison of the phosphorescence spectrum of phthalazine in hydrocarbon and hydroxyl solvents.

From ESR measurements on the phosphorescent state of cinnoline, Vincent and Maki [55] suggest that this is an $n-\pi^*$ triplet state. The present investigation indicates two close lowest triplet states, where, according to calculation I, the $n-\pi^*$ state is the lowest with a $\pi-\pi^*$ state close above, while calculation II yields the reversed order. This is an example of details of spectra for which the present method cannot give a final answer. A similar example can be found for 9,10-diazaphenanthrene. The nature of the triplet states of this molecule has been widely discussed in the literature (see,for instance, Ref. 47, Chapters 3 and 6). In accordance with experimental data, the present method gives two close lying transitions. Calculation I gives $^3B_1$ $(n-\pi^*)$ as the lowest triplet state, while calculation II places $^3B_2$ $(\pi-\pi^*)$ as the lowest triplet, with a state $^3B_1$ only 700 cm^{-1} above $^3B_2$. On the basis of a vibrational analysis of the lowest energy absorption band, Hochstrasser and Marzacco assign the lowest triplet to be a $^3B_2$ transition, followed by a $^3B_1$ transition with an energy gap estimated to be <1400 cm^{-1}. As mentioned previously, the present calculations will give triplet energies up to around 8000 cm^{-1} too low. In order to estimate whether a triplet state lies above or below the lowest singlet state one has consequently to add 8000 cm^{-1} to the published values. Thus, in quinoxaline, as an example, the triplet states $^3B_2$ and $^3B_1$ are predicted to lie below the lowest singlet $^1B_1$, whereas the position of the $^3A_2$ level, relative $^1B_1$ cannot be clearly estimated by the present method. De Groot et al.[56] have experimentally determined the path of entry into and exit from the phosphorescent triplet state $^3B_2$ from measurements of phosphorescence decay after flash excitation and from optical detection of the electron resonance transitions between the spin components. They conclude that the path of intersystem crossing is $^1B_1-^3B_2$ instead of a previous estimate $^1B_1-^3A_2$.[57-58] Lim and Yu [54] make the same conclusion from their phosphorescence spectral data. It would of course be desirable to obtain an experimental determination of the position of the $^3A_2$ band.

Imidazole and purines. Calculated singlet transitions are given in Tables 13 and 14, triplets in Tables 16 and 17. The $\pi-\pi^*$ transitions have been discussed in a recent publication by Fischer-Hjalmars and Nag-Chaudhuri,[22] where also a review of previous experimental and theoretical investigations is given. There are very few observations of $n-\pi^*$ transitions of these molecules. Mason [59] in a review article states that no $n-\pi^*$ transitions have been found in five-membered heteroaromatic molecules. Yet, Braude [60] has published experimental evidence for a weak $n-\pi^*$ singlet of imidazole at around 40 kK. The present calculations give the lowest $n-\pi^*$ singlet in that region well separated from the lowest $\pi-\pi^*$ singlet. The lowest triplet is predicted to be a $\pi-\pi^*$ state. For both 9H-purine and 7H-purine, the calculations give three $n-\pi^*$ singlet transitions below the first $\pi-\pi^*$ singlet. Like Mason,[59] Clark and Tinoco [61] have observed weak bands for 9H-purine at around 34 kK which they assign as due to $n-\pi^*$ transitions, in accordance with the present results. Rich and Kasha [62] also found experimental evidence for an $n-\pi^*$ transition on the long wave length side for biological purines in contrast to the CNDO

results by Giessner-Prettre and Pullman [63],[64] who found the lowest singlet transition to be $\pi - \pi^*$ in nature. Chen and Clark [65] have published polarized reflection spectra of purine crystals. From a simple correction for intermolecular interactions they have deduced approximate free-molecule polarization directions. Their observations are to be compared with calculations on 7H-purine, which is the form for purine in crystal phase. As can be seen from Table 14, the calculations by Fischer-Hjalmars and Nag-Chaudhyri, and the present author are in good agreement with their experimental findings.

The lowest triplet is assigned as [3] $(\pi - \pi^*)$ for both isomers, in accordance with assignments made by Cohen and Goodman.[81]

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