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The Use of the CNDO Method in Spectroscopy

VI. Further $n-\pi^*$ Transitions*

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The Pariser approximation for the two center Coulomb repulsion integrals Γ_{rs} has been replaced by the Nishimoto-Mataga approximation in the original CNDO/S method. This modification has significantly improved the calculated position of the benzene ${}^1B_{1u} \leftarrow {}^1A_{1g}({}^1L_a)$ electronic transition in benzenoid compounds. The calculation of transition moments of $n-\pi^*$ transitions is also considered. These moments vanish formally in any theory employing the ZDO approximation since integrals of the form $\langle 2s|er|2p\rangle$ vanish even when the $2s$ and $2p$ atomic orbitals are on the same center. In this work the ZDO approximation is abandoned in the evaluation of the electronic transition moment resulting in calculated intensities for $n-\pi^*$, ${}^1W \leftarrow {}^1A$, transitions which are in good agreement with experiment.

Die Näherung für die Zweizentrencoulombintegrale nach Pariser in der ursprünglichen Form des CNDO/S-Verfahrens wurde durch die von Nishimoto-Mataga ersetzt, wodurch sich der ${}^1B_{1u} \leftarrow {}^1A_{1g}({}^1L_a)$-Übergang in benzoiden Verbindungen besser ergibt. Die $n-\pi^*$-Übergangsmomente, die bei ZDO-Annahme immer verschwinden, weil dann $\langle 2s|er|2p\rangle$ auch für an gleichen Zentren liegende Orbitale Null ist, werden hier berechnet, und zwar für den ${}^1W \leftarrow {}^1A$-Übergang, wobei die Übereinstimmung mit dem Experiment befriedigend ausfällt.

Introduction

In previous papers [1], a modified CNDO method (CNDO/S) has been developed and used to calculate the electronic spectra of a large number of unsaturated hydrocarbons and heterocycles. It was observed, however, that the ${}^1L_a$ (analogous to the benzene ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition) bands in benzenoid compounds were regularly calculated at an energy 0.8–1.0 eV too low. We have reinvestigated this problem and have found that this discrepancy is largely eliminated by the introduction of the Nishimoto-Mataga approximation [2] to the Coulomb repulsion integrals.

In the original calculations [1], the oscillator strengths [3] for $\pi-\pi^*$ transitions were in good agreement with experiment. However, use of the ZDO approximation makes the electronic transition moments for $n-\pi^*$ transitions formally zero. In the present work, we relax the ZDO approximation by retaining one center integral of the form $\langle 2s|er|2p\rangle$ in the transition moment calculation. These integrals are analogous to those retained by Pople in the calculation of ground state dipole moments [4].

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Parameterization

In the original CNDO/S method, the Coulomb repulsion integrals Γ_{rs} between two centers r and s were approximated according to the original suggestions of Pariser [5]. This approximation has been replaced by the one proposed by Nishimoto and Mataga [2]. If R_{rs} (in atomic units) is the distance between atoms r and s, Γ_{rs} (in atomic units) is given by

$$\Gamma_{rs} = [R_{rs} + 2/(\Gamma_{rr} + \Gamma_{ss})]^{-1} ,$$

where Γ_{rr} are the one-center repulsion integrals obtained from the ionization potentials and electron affinities, as used in our earlier work [1].

The basis set used in these calculations is a set of $2s$ and $2p$ Slater atomic orbitals centered on each second row atom and a $1s$ Slater orbital on each hydrogen atom. The Slater exponents, core integrals, and repulsion integrals used in this calculation are given in Table 1. The ionization potentials and electron affinities used to calculate the core integrals and electron repulsion integrals are those given by Hinze and Jaffé [6]. In the original work [1], the valence states of the various atoms were chosen such that they would be one electron π donors in the molecule. Since this choice is rather restrictive, we have, in the present work, chosen the valence state of carbon as $2s^1 2p^3$, of nitrogen as $2s^2 2p^3$ and oxygen as $2s^2 2p^4$. Such a choice of valence states is much more general than a choice which should be restricted to molecules with π electronic systems. The actual differences between the core integrals and repulsion integrals used in this work and in the original work are quite small and do not significantly affect the calculated spectral properties. Also included in Table 1 are the values of β_r^0 which are the same as previously used, except that β_c^0 has been changed from -17.0 eV to -17.5 eV; the latter value gives, in general, slightly better results. The parameter κ, introduced in previous work, has been retained unchanged. Since some misunderstanding about its significance and its use appears to have arisen in the literature, it is worthwhile to reiterate the nature of the approximation made. The core matrix element $H_{\mu\nu}$ between orbitals μ and ν on centers r and s respectively, is taken proportional to the total overlap between them. However, the overlap between two orbitals μ and ν is evaluated as a sum of two components. One component arises from projection of orbitals μ and ν onto the bond axis, and hence is a σ component, $S_{\mu\nu}^{\sigma}$. The other part arises from the projections of μ and ν normal to the bond axis, and is a π component of overlap, $S_{\mu\nu}^{\pi}$. The element $H_{\mu\nu}$ is then obtained by

$$H_{\mu\nu} = (1/2)(\beta_r^0 + \beta_s^0)(S_{\mu\nu} + \kappa S_{\mu\nu}^{\pi}) .$$

Table 1. Parameters used in CNDO/S method[a]

Atom	H	C	N	O
Slater exponents	1.2	1.625	1.95	2.275
Core integral s	14.35	29.92	40.97	54.51
p	—	11.61	16.96	21.93
Repulsion integral, Γ_{rr}	12.85	10.93	11.88	15.13
β_r^0	-12.0	-17.5	-26.0	-45.0

[a] The core integrals, repulsion integral, and β_r^0 are given in units of eV.

As a consequence of this formulation, $H_{\mu\nu}$ is truly invariant to rotation of the coordinate system.

Calculation of Electronic Transition Moments

The oscillator strength (f) of a transition between two, non-degenerate, electronic states of a molecule is given by

$$f(k,1) = (8\pi^2 mc\nu(k,1)/3he^2)\,[\boldsymbol{M}^*(k,1)\cdot\boldsymbol{M}(k,1)]\ , \tag{1}$$

where $\boldsymbol{M}$ is the transition dipole moment, m and e are the mass and charge of an electron, and ν is the frequency of the transition. The transition moment of an electronic transition in the dipole approximation, expressed in terms of the wavefunction of the initial and final states is

$$\boldsymbol{M}(k,1) = \int \Psi_k^* \sum_p er_p \Psi_1\, dr \equiv \left\langle \Psi_k \middle| \sum_p er_p \middle| \Psi_1 \right\rangle\ , \tag{2}$$

where Ψ_1 and Ψ_k are, respectively, the wavefunctions of the initial and final state, r_p is the position vector of the p'th electron and the summation extends over all electrons. In principle, if the wavefunctions of the two states involved in the transition are known, $\boldsymbol{M}$ may be obtained by direct evaluation of Eq. (2).

Within the framework of the CNDO/S method the wavefunction of the ground state is given by a single Slater determinant, and the excited state wavefunction is a linear combination of spin configurations [1]. The transition moment, $\boldsymbol{M}(k,0)$, can be written, in a general LCAO approximation, as:

$$\begin{aligned}\boldsymbol{M}(k,0) = \sqrt{2}\sum_S \sum_\mu^{(S)} C_{ak}^* c_{\mu i}\Big\{ c_{\mu j'}^* \langle\varphi_\mu|er|\varphi_\mu\rangle + \sum_{\nu\neq\mu}^{(S)} c_{\nu j'}^* \langle\varphi_\nu|er|\varphi_\mu\rangle \\ + \sum_{T\neq S}\sum_\lambda^{(T)} c_{\lambda j'}^* \langle\varphi_\lambda|er|\varphi_\mu\rangle \Big\}\ ,\end{aligned} \tag{3}$$

where the C_{ak}^* are the coefficients of the various spin configurations in the excited state, μ and ν are atomic orbitals on center S and the λ are atomic orbitals on center T.

The strict application of the ZDO approximation to Eq. (3) requires that the integrals in the second and third terms vanish. This leaves only the first term to contribute to $\boldsymbol{M}(k,0)$. At this level of approximation the transition moment for both $\sigma-\pi^*$ and $n-\pi^*$ transitions is identically zero since the product $c_{\mu i}c_{\mu j}$ is always zero for such transitions.

In the present work we shall abandon the ZDO approximation, and retain the first two integrals on the rhs of Eq. (3) in the calculation of the transition moment.

We shall evaluate the first integral on the rhs of Eq. (3) in the manner first suggested by Mulliken and used by us in previous work [1]. The second integral on the rhs of Eq. (3) may be evaluated analytically using Slater orbitals. This integral vanishes except in the case when one of the atomic orbitals is an s orbital and the other is a p orbital. In terms of $2s$ and $2p$ Slater orbitals, this integral is

$$\langle\varphi_s|er_x|\varphi_{p_x}\rangle = \langle\varphi_s|er_y|\varphi_{p_y}\rangle = \langle\varphi_s|er_z|\varphi_{p_z}\rangle = 5ea_0/2\zeta\sqrt{3}\ , \tag{4}$$

where ζ is the orbital exponent of the $2s$ and $2p$ electrons on center S. In Eq. (5) r_x, r_y and r_z are the three cartesian components of the position vector, r, of the electron. All other integrals similar to those given in Eq. (8), such as $\langle\varphi_s|er_x|\varphi_{p_y}\rangle$ vanish.

The x component of the transition moment M of Eq. (7) may now in general be written as

$$M^x(k,0)=\sqrt{2}\sum_{aS}\sum_{\mu}^{(S)} C_{ak}\,c_{\mu i}\left\{c^*_{\mu j'}\,X_S e+\sum_{\nu\neq\mu}^{(S)}\varDelta_{sp_x}c^*_{\mu j'}(5ea_0/2\zeta_S\sqrt{3})\right\}\,, \tag{5}$$

where X_s is the x coordinate of atom S, and

$$\varDelta_{sp_x}=\begin{cases}1 & \mu=\varphi_s\,,\quad \nu=\varphi_{p_x}\quad \text{or}\quad \mu=\varphi_{p_x}\,,\quad \nu=\varphi_s\\ 0 & \text{all other}\quad \mu,\nu\,.\end{cases}$$

The expression for the y and z components of the transition moment are analogous to the expression for the x component, X_S being replaced by Y_S or Z_S and $\varDelta_{sp_x}$ being replaced by $\varDelta_{sp_x}$ or $\varDelta_{sp_x}$ depending on the component being computed. Once the three components of the transition moment vector have been calculated, the entire vector $\boldsymbol{M}$ needed in the evaluation of Eq. (1) is obviously

$$\boldsymbol{M}(k,0)=M^x i+M^y j+M^z k\,.$$

As has been stated above the first term of Eq. (5) vanishes for all transitions of $n-\pi^*$ and $\sigma-\pi^*$ type. The second term vanishes if the transition is forbidden by molecular symmetry. However, this term also vanishes in the case where the state, ${}^1\Psi_k$, is composed entirely of configurations in which the molecular orbital ψ_i is made up of only p atomic orbitals. Platt considers a transition of this type to be forbidden by local symmetry and gives it the notation ${}^1U\leftarrow{}^1A$. The $n-\pi^*$ transitions allowed by local symmetry are symbolized as ${}^1W\leftarrow{}^1A$.

Results and Discussion

Benzene

The ultraviolet spectrum of benzene shows three distinct transitions:

$${}^1B_{2u}\leftarrow{}^1A_{1g},\ {}^1B_{1u}\leftarrow{}^1A_{1g},\ {}^1E_{2u}\leftarrow{}^1A_{1g}\,.$$

In Platt notation [9], these transitions are termed ${}^1L_b$, ${}^1L_a$, ${}^1B$, respectively, and we shall use both the symmetry and Platt notations in this work. Although the original CNDO/S calculations for the first and third transitions were in good agreement with experiment, the ${}^1L_a$ transition was calculated to be at 5.2 eV, compared to an observed value of 6.1 eV.

The inability to properly calculate the energy of this transition has also been observed in PPP calculations whenever the Pariser approximation to Γ_{rs} is used. As we have pointed out [3], the PPP method is a special case of the more general CNDO method; and it is not unexpected that problems arising in one method should also arise in the other. As in the case of PPP calculations, the replacement of the Pariser Γ_{rs} with the Mataga approximation in the CNDO/S significantly improves the calculated position of the ${}^1L_a$ transition, which now is calculated at 6.0 eV. The three benzene transitions given are the lowest three singlet-singlet transitions calculated by the CNDO/S method; i.e., there are no transitions involving $\sigma-\pi^*$ or $\pi-\sigma^*$ states in the region below 6.6 eV.

According to a recent report by Hirota and Nagakura [8], the extension of the configuration interaction calculation to doubly excited configurations in the framework of the PPP method, using the Pariser Γ_{rs} has greatly impoved the energies predicted of ^1L_a transition in benzoid compounds. On the basis of their results, we should expect that the proper inclusion of doubly excited configurations into our original CNDO/S program should lead to similar results.

Pyridine and the Picolines

The electronic spectra of pyridine [9] and the picolines [10, 11] have been the subject of much experimental work over the past two decades. The most logical approach to discussing the spectra of these compounds is first to treat the $\pi-\pi^*$ transition with respect to their relation to benzene, and then discuss the two types of $n-\pi^*$ transitions which appear in the spectra.

The calculated and experimental transition energies and oscillator strength are given in Table 2. In each of the spectra there are four calculated transitions of $\pi-\pi^*$ types in the spectral region above 150 nm. The two lowest energy transitions correspond to the ^1L_b and ^1L_a benzene transitions. Whereas these two

Table 2. The calculated and experimental transition, $\Psi_n \leftarrow \Psi_0$, of pyridine and the picolines[g]

Compound	Type	Symmetry[a]		Energy above ground state (eV)[b]		f[c]	
				cal.	obs.	cal.	obs.
Pyridine[d]	$n-\pi^*$	$^1B_1$	(^1W)	4.2	4.3	0.00	0.003
	$\pi-\pi^*$	$^1B_2$	(^1L_b)	4.9	4.7	0.06	0.030
	$n-\pi^*$	$^1A_2$	(^1W)	5.6	NR	0.0	
	$\pi-\pi^*$	$^1A_1$	(^1L_a)	6.0	6.2	0.22	0.200
	$\pi-\pi^*$	$^1A_1$; $^1B_2$	(^1B)	6.8 (2)	7.0	0.76	1.30
α-Picoline[e,f]	$n-\pi^*$	$^1A''$	(^1W)	4.4	4.3	0.003	0.0019
	$\pi-\pi^*$	$^1A'$	(^1L_b)	4.9	4.6	0.09	0.047
	$n-\pi^*$	$^1A''$	(^1W)	5.4	NR	0.0	
	$\pi-\pi^*$	$^1A'$	(^1L_a)	5.9	NR	0.25	
	$\pi-\pi^*$	$^1A'$; $^1A'$	(^1B)	6.9 (2)	NR	0.79	
β-Picoline[e,f]	$n-\pi^*$	$^1A''$	(^1W)	4.0	4.3	0.003	0.0029
	$\pi-\pi^*$	$^1A'$	(^1L_b)	4.8	4.6	0.080	0.045
	$n-\pi^*$	$^1A''$	(^1W)	5.4	4.4	0.0	W
	$\pi-\pi^*$	$^1A'$	(^1L_a)	5.8	NR	0.204	
	$\pi-\pi^*$	$^1A'$	(^1B)	6.7	NR	0.560	
		$^1A'$		6.9	NR	0.668	
γ-Picoline[e,f]	$n-\pi^*$	$^1A''$	(^1W)	4.3	4.3	0.003	0.0023
	$\pi-\pi^*$	$^1A'$	(^1L_b)	5.0	4.7	0.040	0.032
	$n-\pi^*$	$^1A''$	(^1W)	5.3	NR	0.0	
	$\pi-\pi^*$	$^1A'$	(^1L_a)	6.0	NR	0.108	
	$\pi-\pi^*$	$^1A'$; $^1A'$	(^1B)	6.5 (2)	NR	0.762	

[a] Two symmetries appearing on the same line refer to accidentally degenerate states.
[b] NR, not reported.
[c] W, weak; m, medium; s, strong.
[d] Ref. [9].
[e] Ref. [10].
[f] Ref. [11].
[g] The coordinate system used for the symmetry designations is the same as in Ref. [12].

transitions are symmetry forbidden in benzene, the reduction of molecular symmetry in pyridine and the picolines make these transitions allowed. The calculated values for the transition energies and oscillator strength for ^1L_b band in all four compounds is in good agreement with experiment. Unfortunately, experimental information for the ^1L_a band is available for only pyridine. In this case, the calculated and experimental results are in good agreement.

The highest energy pair of transitions correspond to the two components of the degenerate benzene ^1B transition. In pyridine, α-picoline, and β-picoline, the two components remain degenerate to within the limit to the calculated transition energies. In γ-picoline, the calculations indicate the two components are split by an energy of about 0.2 eV. Experimental transition energies and oscillator strengths are again available for these transitions only in pyridine, and the calculated and experimental results are in good agreement.

The $n-\pi^*$ transitions in pyridine and the three isomeric picolines, all ^1W, can be divided into two groups, in Platt orbital notation [9] $n \rightarrow g$ and $n \rightarrow h$. In order to classify these transitions by symmetry, we consider the methyl group, which probably rotates freely as a pseudoatom; then the $n \rightarrow g$ transitions become $^1B_1 \leftarrow {}^1A_1$ in pyridine and α-picoline, $^1A'' \leftarrow {}^1A'$ in α- and β-picoline, all allowed by molecular symmetry. These, as expected, are the lowest wavelength transitions and are calculated in good agreement with experiment (cf. Table 2). The calculated oscillator strengths, which arise from the non-zero nature of the second term in Eq. (7), are also in good agreement with experiment.

In addition, $n \rightarrow h$ transitions are calculated in all four compounds. They have $^1A_2 \leftarrow {}^1A_1$ symmetry in pyridine and α-picoline, but $^1A'' \leftarrow {}^1A'$ in the α- and β-isomers; consequently, they are forbidden in the first two molecules by molecular symmetry, but allowed in the latter two. These transitions are predicted to occur near 5.5 eV in all four compounds (cf. Table 2). The only suggestion of an observation of this type of transition is due to Sponer and Rush [10] who suggest that they have seen such a transition and have tentatively assigned the 0–0 band to be at 4.4 eV. Since their work, no further work on this band seems to have been reported.

The Diazines: Pyrazine, Pyrimidine, and Pyridazine

The spectra of the three isomeric diazines in the region above 150 nm have received considerable attention. Much of the experimental work has recently been reviewed by Innes [12]. The results of the present calculations along with the experimental result are summarized in Table 3.

Theory suggests that there are two electronic transitions of an $n-\pi^*$ type lying to the long wavelength side of the ^1L_b band in the diazines. Both transitions are $^1W \leftarrow {}^1A$, but one is symmetry allowed while the other is symmetry forbidden in all three compounds. There exists some question in the experimental literature regarding the positions of the 0–0 band for these two transitions. Innes [13] has shown that the two bands chosen by Ito and co-workers [14] in pyrazine were in fact due to the same electronic transition. El-Sayed and Robinson [15], in a low temperature study of the long wavelength region of the diazine spectra, report the observation of both types of $n-\pi^*$ transitions in all three diazines. These authors

Table 3. The calculated and experimental $^1\Psi_n \leftarrow {}^1\Psi_0$ transition in pyrazine, pyrimidine, and pyridazine[d]

Compound	Type	Symmetry	Energy above ground state (eV)[a] cal.	obs.	f[c] cal.	obs.
Pyrazine[b]	$n-\pi^*$	$^1B_{3u}$ (^1W)	3.2	3.8	0.006	0.010
	$n-\pi^*$	$^1B_{2g}$ (^1W)	4.5	3.7	0.0	W
	$\pi-\pi^*$	$^1B_{2u}$ (^1L_b)	4.8	4.8	0.16	0.100
	$n-\pi^*$	^1A_u (^1W)	5.2	NR	0.0	
	$\pi-\pi^*$	$^1B_{1u}$ (^1L_a)	6.3	6.3	0.12	0.145
				6.9		
	$\pi-\pi^*$	$^1B_{1u}$ (^1B)	7.2	7.5	0.48	1.000
	$n-\pi^*$	^1A_u (^1W)	7.2	NR	0.0	
	$\pi-\pi^*$	$^1B_{2u}$ (^1B)	7.5	7.5	0.97	1.000
Pyrimidine[b]	$n-\pi^*$	$^1B_1$ (^1W)	4.2	3.9	0.012	0.0069
	$n-\pi^*$	$^1A_2$ (^1W)	4.6	3.8	0.0	W
	$\pi-\pi^*$	$^1B_2$ (^1L_b)	5.1	5.0	0.07	0.020
	n—π^*	$^1A_2$ (^1W)	5.6	NR	0.0	
	$\pi-\pi^*$	$^1A_1$ (^1L_a)	6.1	6.5	0.11	0.100
	$n-\pi^*$	$^1B_1$ (^1W)	6.4	6.4	0.005	0.005
	$n-\pi^*$	$^1A_2$ (^1W)	7.0	NR	0.0	
	π-Rydberg			7.0		
	$\pi-\pi^*$	$^1B_2$ $^1A_1$ (^1B)	7.1 7.1	7.3 7.2	0.62 0.63	1.000
Pyridazine[b]	$n-\pi^*$	$^1B_1$ (^1W)	3.3	3.3	0.008	0.0058
	$n-\pi^*$	$^1A_2$ (^1W)	4.4	2.3	0.0	W
	$\pi-\pi^*$	$^1B_2$ (^1L_b)	5.1	4.9	0.05	0.030
	$n-\pi^*$	$^1A_2$ (^1W)	5.6	NR	0.0	
	$\pi-\pi^*$	$^1A_1$ (^1L_a)	6.1	6.2	0.11	0.200
	$n-\pi^*$	$^1B_1$ (^1W)	6.2	6.4	0.005	W
	$\pi-\pi^*$	$^1B_2$ $^1A_1$ (^1B)	6.9	7.1	0.69 0.61	1.300

[a] NR, not reported.

[b] Ref. [12].

[c] W, weak.

[d] The coordinate system used for the symmetry designations is the same as in Ref. [12].

have also calculated the expected separation between the two excited singlet states, assuming that the nitrogen lone-pair could be represented in terms of a localized orbital. The results of a recent semi-empirical calculations reported by Kato *et al.* [16], and of an *ab initio* calculation on pyrazine reported by Hackmeyer and Whitten [17] agree with our calculations in predicting that the symmetry forbidden transition should be expected to lie at higher energies than the symmetry allowed transition in all three compounds. The calculated splitting and the experimental results of El-Sayed indicate just the opposite order. We have been unable to find any other experimental results which might help clarify this situation. More experimental work on the nature of the spectral bands in the diazines is certainly indicated.

The three sets of calculation on pyrazine all show a rather large energy gap between the upper states of the symmetry allowed and forbidden transitions. This gap can be ultimately traced to the very large splitting between the two molecular orbitals containing the positive and negative combination of nitrogen "lone-pair" atomic orbitals. A better understanding of this result is facilitated by a more detailed examination of the "lone-pair" molecular orbitals.

We can visualize these MO's as formed by linear combination of hybrid AO's n_1 and n_2, of the two nitrogen atoms, but we must recognize that other AO's may also enter into the MO, as determined by the SCF procedure. The two MO's will be called n_+ and n_-, the former containing the combination $n_1 + n_2$, the latter, $n_1 - n_2$. In pyrazine, with D_{2h} symmetry, n_+ belongs to a_g, n_- to b_{1u}; in the other two diazines, with C_{2v} symmetry, n_+ still belongs to the totally symmetric representation a_1, and n_- belongs to b_2. In the SCF procedure, the symmetry adapted

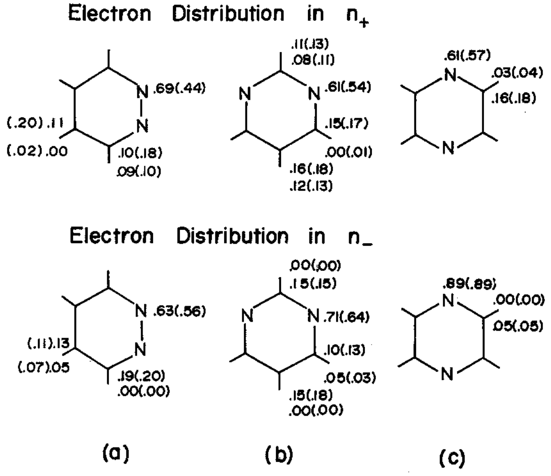

Fig. 1. The electron delocalization in the n_+ and n_- molecular orbitals of (a) pyridazine, (b) pyrimidine and (c) pyrazine

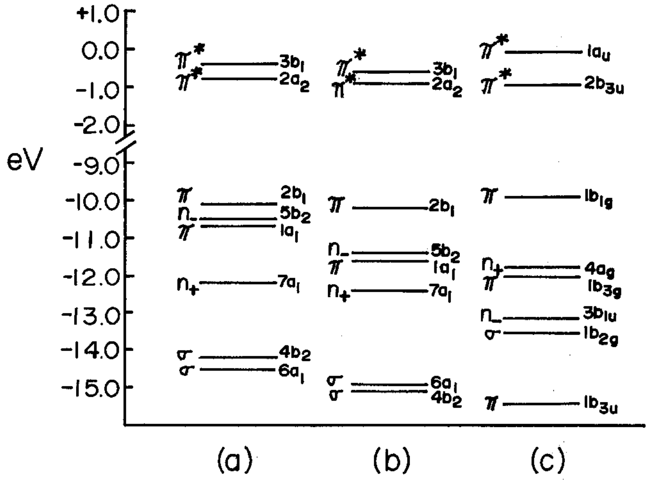

Fig. 2. Molecular orbitals of (a) pyridazine, (b) pyrimidine and (c) pyrazine

combinations n_1+n_2 and n_1-n_2 combine with any other symmetry adapted combination of the carbon and hydrogen orbitals. This causes the "lone-pair" electrons to be delocalized to a greater extent than is the case when n_+ and n_- are pure "lone-pairs". A comparison of the delocalization in the present work and the original work of Del Bene and Jaffé [1] is made in Fig. 1. As can be seen, the delocalization of the lone-pair electrons is somewhat greater where the Mataga approximation is used.

Another interesting feature of the diazene MO's is revealed when we inspect Fig. 2. This figure shows schematically the position of the six highest energy occupied molecular orbitals along with the two lowest energy virtual orbitals. If we compare the position of n_+ and n_- in the three compounds, we immediately see that in pyrimidine and pyridazine n_- is the highest energy of the two, while in pyrazine n_+ is the highest. The order of n_+ and n_- in pyrazine as predicted by the CNDO/S calculation is in agreement with the order predicted by recent *ab initio* calculation of Whitten [17] and of Clementi [18]. There are no *ab initio* calculations available for pyrimidine and pyridazine with which to compare the CNDO/S results[1].

Table 4. The calculated and observed $^1\Psi_n \leftarrow {}^1\Psi_0$ transitions in *s*-triazine and *s*-tetrazine[b]

Compound	Type	Symmetry	Energy above ground state (eV)		f	
			cal.	obs.	cal.	obs.
s-Triazine[a]	$n-\pi^*$	$^1E''$ (^1W)	4.5	4.0		
	$n-\pi^*$	$^1E''$ (^1W)	4.5	4.0	0.0	
	$n-\pi^*$	$^1A_2''$ (^1W)	4.6	3.9	0.027	0.018, 0.024
	$n-\pi^*$	$^1A_2''$ (^1W)	5.1		0.0	
	$\pi-\pi^*$	$^1A_1'$ (^1L_b)	5.6	5.5	0.0	0.002
	$\pi-\pi^*$	$^1A_2''$ (^1L_a)	6.6		0.0	
	$\pi-\pi^*$	$^1E^1$ (^1B)	7.2		0.62	
					0.62	
s-Tetrazine[a]	$n-\pi^*$	$^1B_{3u}$ (^1W)	2.6	2.3	0.018	0.004
	$n-\pi^*$	^1A_u (^1W)	4.3	3.9	0.0	0.001
	$n-\pi^*$	$^1B_{1g}$ (^1W)	4.3			
	$\pi-\pi^*$	$^1B_{2u}$ (^1L_b)	4.9	4.3	0.15	
	$n-\pi^*$	B_{2g} (^1W)	5.1			
	$n-\pi^*$	A_u (^1W)	5.4			
	$\pi-\pi^*$	B_{1u} (^1L_b)	6.6		0.02	
	$n-\pi^*$	B_{3u} (^1W)	6.7		0.01	
	$\pi-\pi^*$	B_{1u} (^1B)	7.3		0.89	
	$\pi-\pi^*$	B_{2u}	7.8		0.52	

[a] Ref. [12].

[b] The coordinate system used for the symmetry designations is the same as in Ref. [12].

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[1] We wish to thank the referee for pointing out that the order of the MO's given in Fig. 2 is not in agreement with the order determined by R. Gleiter, E. Heilbroner, and V. Horminey using photoelectron spectroscopy [Angew. Chem. **82**, 878 (1970)]. Since the CNDO/S method is parameterized to yield information about excited states, disagreement on the position of individual MO's is not too surprising. However, before commenting we wish to look at this problem in greater detail.

s-Triazine, s-Tetrazine

The spectra of *s*-triazine and *s*-tetrazine have been less intensively studied than the diazines, but we include the calculated and experimental results for the sake of completeness. The calculated and experimental spectra of these molecules are given in Table 4.

The ^1L_b transition is the only benzenoid transition reported in the two compounds. Inspection of Table 4 shows that the calculations are in good agreement with experiment. In the case of *s*-triazine, the ^1L_b transition is forbidden by molecular symmetry. As a consequence, the calculated oscillator strength is zero. In accordance with the symmetry forbiddenness of this transition, the experimental oscillator strength is small, being about the same size as in benzene itself. In the case of *s*-tetrazine, the singlet ^1L_b transition is symmetry allowed. The calculated oscillator strength ($f = 0.15$) has about the same magnitude as the value for the corresponding quantity in the diazines.

The number of lone-pair electrons in these two compounds implies that we should expect a considerable number of transitions corresponding to the promotion of lone-pair electrons. Of the many possible transitions, only the lowest energy transition in each of the two compounds have been observed. The calculated value in *s*-triazine is in fair agreement with experiment, and in *s*-tetrazine, the calculations are in good agreement with experiment.

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