

Triplet States via Intermediate Neglect of Differential Overlap: Benzene, Pyridine and the Diazines

Joan E. Ridley and Michael C. Zerner

*Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry,
University of Guelph, Guelph, Ontario, Canada*

The intermediate neglect of differential overlap technique is modified and applied to the calculation of excited triplet states. The resulting method generally reproduces the transition energies of the better-classified observations within a rms error of 1000 cm^{-1} . Trends are well reproduced, and the calculated orders of $n-\pi^*$ and $\pi-\pi^*$ triplet states are in good accord with the experimental information to date.

The method is applied to benzene and the azines. The lowest four triplet states of benzene are calculated in good accord with experiment. Pyridine is calculated to have a $n-\pi^*$ triplet nearly degenerate with the lowest lying $\pi-\pi^*$ triplet, corroborating suggestions of Japar and Ramsay based on experimental information. A detailed analysis is made of the diazines, and assignments are suggested for the higher lying triplet states not yet classified or not yet observed.

Key words: Triplet states, INDO calculations of \sim - Benzene - Pyridine - Diazines

1. Introduction

In the calculation of electronically excited states of molecules two general approaches have dominated; the Virtual Orbital Configuration Interaction method (VOCI) and the "energy difference" (ΔE) method. In the VOCI method the ground state is approximated by a single determinant (or a proper spin projection), built up of the N lowest energy molecular orbitals, generally but not always, of the self-consistent field type, where N is the number of electrons. A basis of excited configurations is then built by exciting one or more electrons from these occupied orbitals to the virtual, or unoccupied, orbitals, and these configurations are then used as the basis to describe molecular excited states as well as to improve the description of the ground state.

An immediate advantage of this technique is that it provides an easy algorithm for calculating several of the lowest-lying excited states at one time. The disadvantage, however, lies in the fact that the occupied orbitals being used to describe the excited state have been optimized for the ground state. In addition, the virtual orbitals being populated are appropriate not for the N electron system, but the $N + 1$ (negative ion) system [1], and are, in general, too diffuse. The net result is the generation of configurations that do not always provide a "good" starting point for the description of an excited state of interest, necessitating the inclusion of a great many determinants in the configuration interaction expansion, as well as an enlarged basis of orbitals. Nevertheless, a great wealth of knowledge has been

built by experience with this technique, and the excited states of many small and even some quite large molecules have been accurately examined by *ab initio* methods.

In the "energy difference" technique two separate calculations of similar accuracy are performed, one on the ground state, one on the excited state of interest, and the transition energy obtained by subtraction. Generally these calculations are of the Hartree-Fock self-consistent field type, but they need not be. The advantage of this technique is that each state is separately optimized and that electronic rearrangements and relaxations are "built-in". Apparent disadvantages are that a separate calculation is required for each excited state, and that transition energies, small numbers, are obtained from the subtraction of two large numbers. With regard to the latter, difficulty may be encountered in trying to ascertain that each separate calculation is of "comparable" accuracy. For example, whereas the ground state of a molecule is well separated from excited states, and may reasonably be represented by a single determinant (or proper spin combination), excited states are often not. If both calculations are of the restricted type [2], the ground state may be better treated than the excited states. If excited states are calculated in the unrestricted formalism [3], they may be relatively better treated than the ground state [4, 5]. These disadvantages standing, the ΔE method is capable, if cleverly pursued, of great accuracy and has received considerable attention especially in the calculation of ionization processes where relaxation may be of prime importance [6, 7, 8].

Calculations of excited states by semi-empirical MO theories have nearly always been of the VOCI type. Early successes of π systems utilizing Pariser-Parr-Pople theory quickly brought order to much of the π - π^* spectra of hydrocarbons [9]. More recently the Complete Neglect of Differential Overlap technique, CNDO, [10] was modified by Del Bene and Jaffé and applied to the calculation of excited states [11]. Modifications of this basic technique by Ellis, Kuehnlenz and Jaffé [12], and an Intermediate Neglect of Differential Overlap, INDO, refinement introduced by ourselves [13] have proven remarkably accurate in predictions on excited singlet states that do not possess a great amount of Rydberg character.

Although the CNDO/INDO VOCI model has proven very reliable in applications involving singlet states, predictions on triplet states have not been as successful. Jaffé and coworkers [14] have examined both VOCI and ΔE techniques in attempts to classify triplet states. Their VOCI model is similar to that which they utilize for singlets [12]; their ΔE technique involves two calculations of the restricted Hartree-Fock type. The results of neither are totally satisfactory; thus they have adopted an "extrapolation" method that uses the energies of the pure configurations from the ΔE calculation, and the expansion coefficients from the VOCI calculation [14]. The results are better, but still not nearly as impressive as results obtained for singlets.

It seems to us that this extrapolation procedure is more complex than need be. Although we would also admit to such a procedure if we found it necessary, *ab initio* work by Del Bene, Ditchfield and Pople [15] strongly suggests that the triplet spectra ought to be *easier* to calculate by VOCI than the corresponding singlets.

In this report we re-examine the virtual orbital configuration interaction technique for triplets using the INDO technique developed previously. The method is then applied to benzene, pyridine and the diazines. A comparison of the calculated transition energies with the better classified experimental bands of these compounds, as well as others not here reported [16] suggests a rms error of $\sim 1000 \text{ cm}^{-1}$, for most cases comparable with the

accuracy of the experiment, and about as reliable as results obtained in our singlet studies [13, 17]. A good comparison between this theory and experiment is, however, not available for most often only the lowest excited triplet of a species is observed.

2. Model

The basic model we adopt for calculating triplet states is essentially a reparameterization of the INDO/S method [13] used for singlets and applied to azines [13] and azanaphthalenes [17]. It is useful here to outline some of the modifications of the Intermediate Neglect of Differential Overlap (INDO) model of Pople, Beveridge and Dobosh [18] that we utilized in the study of singlets [13] to more clearly introduce the triplet parameterization.

A self-consistent field calculation is performed on the ground state to generate molecular orbitals that are then entered into a configuration interaction calculation of the lowest-lying excited states.

In the procedure it was found advantageous to employ a formula for the "resonance integral" β of the Mulliken form [10, 18, 19]

$$\beta_{\mu\nu} = \bar{\beta}_{AB} \bar{S}_{\mu\nu} \quad \mu \in A, \quad \nu \in B \quad (1)$$

where $\bar{\beta} = (\beta_A + \beta_B)/2$ and β_A and β_B are empirical constants characteristic of atom A and of atom B [10]. $\bar{S}_{\mu\nu}$ is a "weighted" overlap decreasing the π - π interactions [11, 13] and increasing the σ - σ interactions [13], i.e.

$$\begin{aligned} \bar{S}_{ss'} &= \Delta_{ss'} \\ \bar{S}_{sp'} &= g_{s\sigma'} \Delta_{sp'} \\ \bar{S}_{pp'} &= g_{\sigma\sigma'} f_{\sigma\sigma'} \Delta_{\sigma\sigma'} + g_{\pi\pi'} f_{\pi\pi'} \Delta_{\pi\pi'} \end{aligned} \quad (2)$$

In Eq. (2) $\Delta_{\mu\nu}$ is the atomic orbital overlap, $g_{\mu\nu}$ the angular factor necessary to rotate back from the local diatomic system between atoms A and B to the molecular system, and $f_{\sigma\sigma'} = 1.267$ and $f_{\pi\pi'} = 0.585$, those factors necessary to increase the $\sigma\sigma'$ interactions and decrease the $\pi\pi'$ interactions to give best agreement with experimental studies. The Coulomb integral was evaluated using the Weiss [20] modification of the Mataga-Nishimoto Equation [21],

$$\begin{aligned} \gamma_{\mu\nu} &\equiv (\mu\mu|\nu\nu) \equiv \int d\tau_1 d\tau_2 \chi_{\mu}^*(1) \chi_{\mu}^*(1) r_{12}^{-1} \chi_{\nu}(2) \chi_{\nu}(2) \\ &= \frac{f_{\gamma}}{f_{\gamma}(\gamma_{\mu\mu} + \gamma_{\nu\nu})^{-1} + R} \end{aligned} \quad (3)$$

with f_{γ} set to 1.2.

We adopted the INDO model over the CNDO model, for by including one centre exchange integrals the excitation energies of σ - π^* and π - σ^* transitions of different multiplicities are split as, indeed, they should be. Although we found it necessary to introduce a separate parameterization for the triplets, described below, we have not found any parameterization for the CNDO model which is as successful as the INDO technique described. The CNDO model presented us with several important π - π^* , n - π^* triplet state reversals. Indeed, the CNDO model did not allow us to successfully explain the spectra of some of the diazines, or the photochemistry of the paraquinones that originally motivated this study [16].

It is, perhaps, not surprising to find that a model so finely tuned to present accurate singlet state transition energies is far less successful in its predictions on triplet states. If we suppose that our parameterization is one to yield the best compromise molecular orbitals for singlet states (compromise between molecular orbitals describing *all* singlet states examined, including the ground state), then should we not search for those most appropriate for all triplets? With this in mind, the calculation of the Coulomb integrals, Eq. (3), is most suspect since the electron correlation that is empirically included by parameterizing on experimental spectra ought to be principally through two electron terms, and triplets might, in general, be expected to have less correlation than singlets. Examination of atomic calculations of near Hartree-Fock accuracy [22] shows that effective one-centre Coulomb integrals (Slater-Condon F° 's) are not highly sensitive to spin state: differences are of the same order as differences between $F^{\circ}(ss)$, $F^{\circ}(sp)$ and $F^{\circ}(pp)$, all assumed by this treatment to be the same,

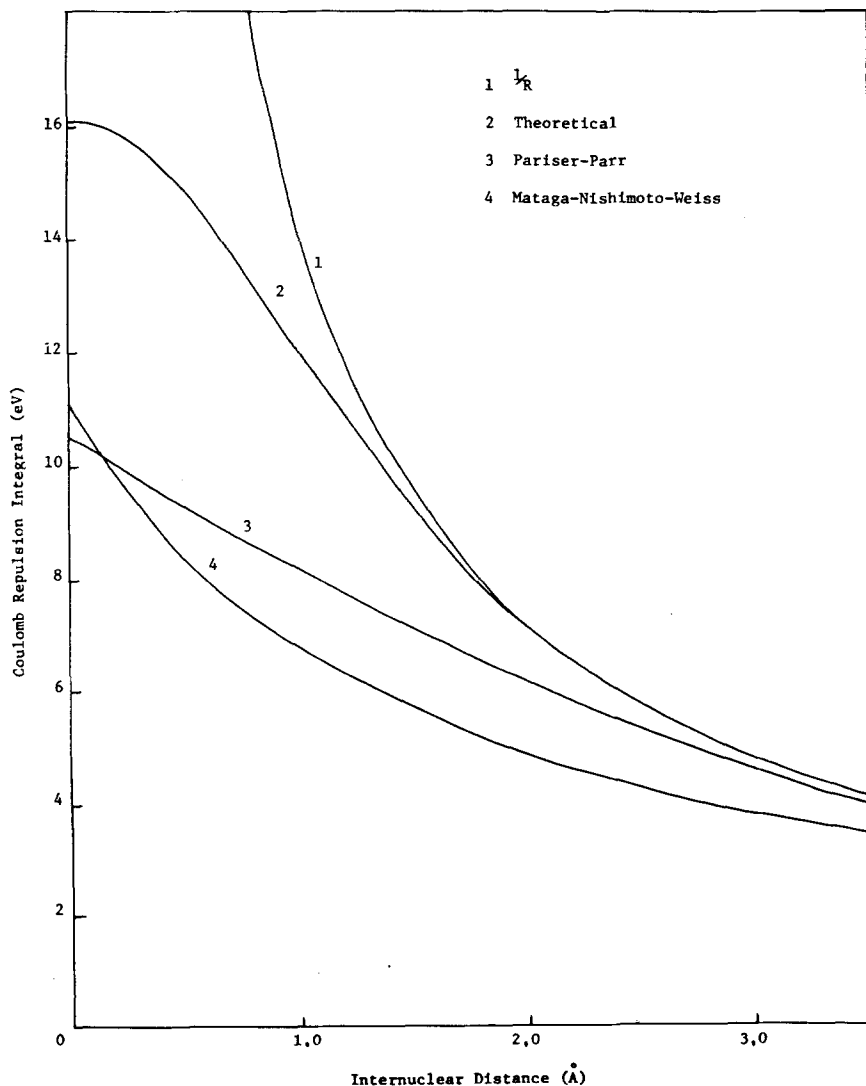


Fig. 1. Distance Dependence of Two Electron Coulomb Integrals. No. 3, Pariser-Parr, was used for calculating Triplet Spectra while No. 4, Mataga-Nishimoto Weiss was used for calculating Singlets

and a function only of atom. We thus examine the distance dependence of $\gamma_{\mu\nu}$, and expect a slower decrease with increasing distance between the two centres. After examining Eq. (3) with f_γ increased, a theoretical integral with scaled atomic orbital exponent to reproduce the one centre values, and the Pariser-Parr formula [23], for all integrals we adopt the latter as most adequate; i.e. with Z_p the effective nuclear charge

$$R > 2.8 \text{ \AA}: \gamma_{\mu\nu} = \{ [1 + [(r_p - r_q)/2R]^2]^{-1/2} + [1 + [(r_p + r_q)/2R]^2]^{-1/2} \} / 2R$$

$$r_p = (8.687/Z_p) \quad (4)$$

$$R < 2.8 \text{ \AA}: \gamma_{\mu\nu} = (\gamma_{\mu\mu} + \gamma_{\nu\nu})/2 - aR - bR^2$$

of atom p obtained from Slater's Rules [24]. The distance dependence of γ is compared in Fig. 1 for those functions giving the best results for singlets and triplets. A re-examination of resonance integrals β_A , one centre Coulomb integrals, γ_{00} 's (F^{00} 's), and $f_{\sigma\sigma}$ and $f_{\pi\pi}$ shows that only $f_{\pi\pi}$ need be significantly changed from the singlet parameterization, and is increased to 0.680. The reason for this is not clear. The γ_{00} for C and N are the "traditional" values of Pariser and Parr [23]¹. The calculated triplet spectra have not been found very sensitive to reasonable choices in γ_{00} and this choice leads to a satisfactory split between the lowest $n-\pi^*$ triplets and their corresponding singlets. A summary of the triplet parameterization is given in Tables 1 and 2.

A great many studies lend support for methods such as this one that attempt to include the effects of higher excitations through a parameterized scheme of single excitations only. The recent *ab initio* calculations on benzene by Hay and Shavitt [25], for example, show that for many states, excitation energies calculated from singles only are in good agreement with those from a very large CI of singles, doubles and triples; while CI of singles and doubles alone gives considerably higher results (due mostly to lowering of the ground state). In addition, inclusion of only doubles is expected to "unbalance" the calculation in a predictable fashion [26]. To improve upon the singles-only calculation an extensive treatment

Table 1. Parameterization

Parameter	Singlets	Triplets	
γ_{00}	H	12.85 eV	12.85 eV
	C	11.11 eV	10.50 eV ^c
	N	12.01 eV	12.47 eV ^c
	O	13.00 eV	13.00 eV
β	H	-9.00 eV	-9.00 eV
	C	-17.00 eV	-17.00 eV
	N	-26.00 eV	-26.00 eV
	O	-34.00 eV	-34.00 eV
$f_{\sigma\sigma}$	1.267	1.267	
$f_{\pi\pi}$	0.585	0.680	
$\gamma(R)$	Mataga-Nishimoto-Weiss, $f_\gamma = 1.2^a$	Pariser-Parr ^b	

^a See Eq. 3. ^b See Eq. 4 and Table 2.
^c Traditional values, Ref. [23].

¹ This is a formula originally intended for pi orbitals, but requirements for rotational invariance necessitate that Coulomb integrals be functions only of the atoms involved, and not a function of orbital.

Table 2. Values of "a" and "b" parameters for the calculation of Coulomb integrals from the Pariser-Parr formula

Atom pair	a	b
H-H	4.833	-0.608
C-C	2.606	-0.213
N-N	3.764	-0.384
O-O	4.046	-0.423
C-H	3.997	-0.478
N-H	4.609	-0.572
O-H	4.781	-0.600
C-N	3.189	-0.299
C-O	3.332	-0.319
N-O	3.906	-0.404

involving the additional inclusion of doubly and triply excited configurations (i.e. doubly excited with respect to the singles) is necessary to provide a balanced CI and results as consistent with experiment as a parameterized theory of single excitations only.

Such a theory of single excitations can, of course, not account for states that are principally double excitations in nature. This shortcoming may limit the utility of this approach to molecules that are not so large that such excitations occur in the visible or near UV.

As was discussed previously we choose, when possible, to compare calculated energies to experimental band maxima, ν_{\max} [13].

3. Procedures

The calculations reported here are on benzene, pyridine, and the three diazines, Fig. 2. A study of the photocycloaddition of alkenes to paraquinones is reported elsewhere [16]. A ground state calculation is performed with the triplet parameterization from an input of molecular geometry and atomic numbers. The molecular orbitals obtained are then used to generate pure singly excited configurations.

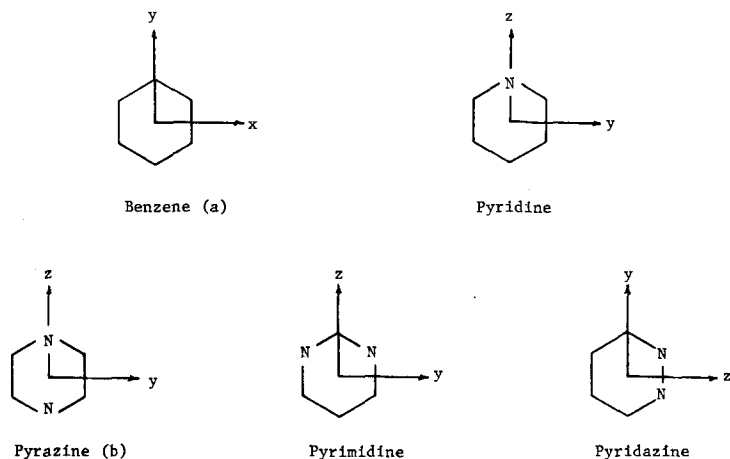


Fig. 2. Molecules of this Study and their Coordinate Systems. Footnotes refer to crystal structures: (a) G. E. Bacon, N. A. Curry and S. A. Wilson, Proc. Roy. Soc. 279A, 98 (1964). (b) P. J. Wheatley, Acta Cryst. 10, 182 (1957)

Table 3. Benzene

Observed			Calculated		
Symm.	Type	Energy (cm ⁻¹)	Symm.	Type	Energy (cm ⁻¹)
³ B _{1u}	π-π*	31,860 ^a	³ B _{1u}	π-π*	31,464
³ E _{1u}	π-π*	38,310 ^a	³ E _{1u}	π-π*	39,353
³ B _{2u}	π-π*	45,170 ^a	³ B _{2u}	π-π*	43,905
³ E _{2g}	π-π*	~52,800 ^b	³ E _{2g}	π-π*	56,950

^a Ref. [30]. Electron impact study.

^b Ref. [31]. In alkane and alcohol solutions.

The process of choosing excited configurations for the configuration interaction is considerably more difficult for the case of triplets than for singlets. The triplet states appear far more sensitive to very high-lying states of appropriate symmetry.

We have discovered no systematic method for choosing M highest occupied and M lowest empty molecular orbitals to generate configurations for the triplet CI [15, 27]. Rather it has been found necessary to break the CI into a π-π*, σ-σ* part and a σ-π*, π-σ* part and include *all* pi symmetry molecular orbitals in generating determinants. Relatively few of the possible σ type molecular orbitals need be considered before stability sets in: generally 4 or 5 occupied, 2 or 3 virtual. In addition, σ-σ* states have been found to mix only very slightly with π-π* states for molecules the size of those we are examining here, and they have not been included except for the initial trial runs. Caution, however, must be exercised with smaller systems where π-π* states are higher lying in energy, and thus close in energy to σ-σ* states [28, 29].

4. Results

4.1. Benzene

Benzene calculations were used to test various parameterizations. The method adopted, and especially the choice of the Pariser-Parr γ , gave the best results when compared with experiment, Table 3. The agreement between observed [30, 31] and calculated bands is

Table 4. Benzene - triplets: Comparison with *ab initio* CI study

State	Expt.	INDO/S	<i>ab initio</i> ^a		
			Singles	Singles and doubles	Singles and doubles and triples
³ B _{1u}	3.9	3.90	3.67	5.20	3.83
³ E _{1u}	4.7	4.88	5.15	5.78	4.98
³ B _{2u}	5.6	5.44	6.01	7.76	7.00
³ E _{2g}	6.55	7.06	7.86	8.59	7.28

^a Ref. [25].

Table 5. Benzene: All triplets below 10 eV

${}^3B_{1u}$	3.90	$\pi-\pi^*$
${}^3E_{1u}$	4.88	$\pi-\pi^*$
${}^3B_{2u}$	5.44	$\pi-\pi^*$
${}^3E_{2g}$	7.06	$\pi-\pi^*$
${}^3E_{2u}$	7.18	$\pi-\sigma^*$
${}^3B_{2g}$	7.52	$\pi-\sigma^*$
${}^3E_{1g}$	8.05	$\pi-\sigma^*$
${}^3E_{2u}$	8.25	$\sigma-\pi^*$
${}^3A_{2u}$	8.33	$\sigma-\pi^*$
${}^3A_{1u}$	8.50	$\sigma-\pi^*$
${}^3B_{1g}$	8.54	$\pi-\sigma^*$
${}^3A_{2u}$	9.94	$\pi-\sigma^*$
${}^3E_{1g}$	10.00	$\pi-\sigma^*$

quite good. It should be noted that the experimental value for the ${}^3E_{2g}$ is that found in solution; it might therefore lie higher in gaseous benzene.

A comparison of our INDO results with those from the *ab initio* calculations of Hay and Shavitt [25] for the four observed $\pi-\pi^*$ states is presented in Table 4. The most striking difference appears in the third (${}^3B_{2u}$) band where our value is 0.16 eV below the experimental value, the *ab initio* value 1.40 eV above. Table 5 contains a tabulation of calculated transition energies lying below 10 eV.

Although the ground state SCF calculation is meant only to supply molecular orbitals suitable for the triplet CI and a reference energy, a comparison of orbital energies computed from the calculation for singlets is interesting, Table 6. In general, differences are not great; not surprisingly, the singlet parameterization appears to provide eigenvalues in better agreement with *ab initio* calculations and ionization information *via* Koopmans' approximation [32].

4.2. Pyridine

The calculated and observed triplet energies of pyridine are presented in Table 7.

Two recent experimental studies of the triplet absorption in pyridine are available. Doering and Moore [33] observed a single singlet-triplet transition, in gas phase pyridine by ion

Table 6. Orbital energies for benzene (eV)

Triplet parameterization	Singlet ^a parameterization	<i>Ab initio</i> ^b	Ionization potentials ^c	
10.18	9.0	9.25	9.24	$1e_{1g}(\pi)$
12.95	12.6	13.41	11.5	$3e_{2g}$
15.36	13.4	13.74	12.3	$1a_{2u}(\pi)$
16.03	15.3	16.10	13.8	$3e_{1u}$
18.51	17.3	16.95	14.7	$1b_{2u}$
17.91	17.5	17.46	15.4	$2b_{1u}$
24.72	23.6	19.48	16.9	$3a_{1g}$
26.20	25.1	22.50	19.2	$2e_{2g}$
33.88	32.7	27.79	22.8	$2e_{1u}$

^a Ref. [13]. ^b Ref. [25]. ^c Ref. [32].

Table 7. Pyridine

Observed			Calculated		
Symmetry	Type	Energy (cm ⁻¹)	Symmetry	Type	Energy (cm ⁻¹)
³ A ₁	π-π*	33,100 ± 800 ^a	³ A ₁	π-π*	33,001
		[29,800 ^b]	³ B ₁	n-π*	33,223
		31,250 – 33,300 ^b	³ B ₂	π-π*	37,074
			³ A ₁	π-π*	40,994
			³ A ₂	n-π*	45,010

^a Ref. [33]. ν_{\max} value. ^b Ref. [34]. See text.

and electron impact, with onset at $\sim 30,600$ cm⁻¹ and maximum at $\sim 33,100$ cm⁻¹. They find no evidence for any lower lying triplet states. Japar and Ramsay [34] report the observation of two distinct band systems in this region, differing by 1,700 cm⁻¹. Arguing that this interval is larger than the known vibrational frequencies of pyridine, with the possible exception of some CH modes, they assign the lower with onset at $\sim 29,700$ cm⁻¹ to ³A₁(π-π*), the second system, between $\sim 31,250$ cm⁻¹ and 33,300 cm⁻¹ to either ³B₁(n-π*), ³A₂(n-π*) or ¹A₂(n-π*).

We calculate the lowest triplet transition of pyridine to be ³A₁(π-π*) at 33,001 cm⁻¹. This result is in excellent agreement with the ν_{\max} of Doering and Moore. A second band of ³B₁(n-π*) type, however, is calculated to lie within ~ 223 cm⁻¹ of the first, corroborating the suggestion of Japar and Ramsay that two separate systems may lie close. The next highest calculated state is the first singlet, ¹B₁(n-π*), calculated and observed at 35,568 cm⁻¹ [13].

The first state of ³A₂(n-π*) symmetry we calculate at 45,010 cm⁻¹; the first ¹A₂ at 44,800 cm⁻¹. It seems unlikely that either of these are candidates for the second system observed by Japar and Ramsay; most likely it is that the first two triplets are ³A₁(π-π*) and ³B₁(n-π*), calculated to lie so close in energy that we can only suggest that the ³A₁(π-π*) is the lower.

Hoover and Kasha [35] have suggested on the basis of phosphorescence studies that the ³A₂(n-π*) is the lowest triplet. We find this unlikely, as we calculate this state greater than 12,000 cm⁻¹ higher than the lowest lying ³A₁(π-π*). Similarly no evidence for the corresponding ¹A₂(n-π*) has been found, at least below $\sim 38,000$ cm⁻¹, and singlet-triplet splittings between n-π* states are seldom greater than $\sim 2,000$ cm⁻¹. The closeness of our calculated ³A₁(π-π*) and ³B₁(n-π*) levels however is consistent with their observations on substituted pyridines, 2,6-dimethyl substitution on pyridine would be expected to lower the ³A₁(π-π*) relative to the ³B₁(n-π*); the observed phosphorescence lifetime is 3.2 seconds, comparable to the benzene phosphorescence which is clearly π-π*. 4-cyano substitution would lower the ³B₁(n-π*) relative to the ³A₁(π-π*); the lifetime observed is 0.004 seconds, a value typical of n-π* phosphorescence. Why pyridine itself shows no phosphorescence may be due to interactions of these two levels calculated nearly degenerate.

4.3. Diazines

Calculations have been performed on the triplet spectra of the diazines: pyrazine (1,4-diazine), pyrimidine (1,3 diazine) and pyridazine (1,2 diazine). All have calculated and

Table 8. Pyrazine

Observed			Calculated			
Symmetry	Type	Energy (cm ⁻¹)	Symmetry ^b	Type ^b	Energy (cm ⁻¹) ^b	<i>ab initio</i> ^c (cm ⁻¹)
³ B _{3u}	<i>n</i> -π*	26,818 ^a	³ B _{3u}	<i>n</i> -π*	26,157	28,715
			³ B _{2u}	π-π*	32,481	43,476
			³ B _{1u}	π-π*	33,710	33,150
			³ B _{2g}	<i>n</i> -π*	35,976	40,249
			³ A _u	<i>n</i> -π*	41,774	41,459
			³ B _{1u}	π-π*	43,515	43,637

^a Ref. [37]. ^b This work. ^c *Ab initio* results of Hackmeyer and Whitten, Ref. [38].

observed lowest triplet bands of *n*-π* character (corresponding to their lowest singlet transitions). In each case the order of the allowed and forbidden ³*n*-π* transitions is calculated to be identical to that of the ¹*n*-π*s.

The intensity of observed phosphorescence in the series varies greatly from the intense emission of pyrazine, less intense of pyrimidine, to no emission observed for pyridazine.

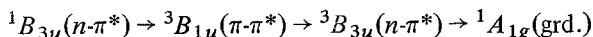
It may be noted that only the pyrazine structure has been determined experimentally [36]. The input geometries of pyrimidine and pyridazine have been estimated by extrapolation from other known molecules. The calculated spectrum of pyridazine is sensitive to the N-N bond length. We have adjusted this length to give good agreement between calculated and experimental singlet transitions, as discussed below.

4.3.1. Pyrazine

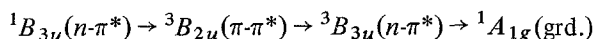
Table 8 contains the results found for the triplet spectrum of pyrazine. Only one triplet, assigned ³B_{3u}(*n*-π*) has been observed at 26,818 [37]; the calculation is in good agreement with a prediction at 26,200 cm⁻¹. Other calculated bands are listed in the table.

Results found in the *ab initio* study of pyrazine by Hackmeyer and Whitten [38] are compared with our INDO/S results in Table 8. The energies calculated by the two methods are in good agreement with the single exception of the ³B_{2u}(π-π*) state which is calculated by the INDO/S technique to lie ~11,000 cm⁻¹ below the *ab initio* prediction.

The second triplet state of pyrazine has been identified as ³B_{1u} by indirect evidence [39]. It has been postulated as the intermediate state in the intersystem crossing mechanism for phosphorescence



through the τ_y(*b*_{2g}) spin function. Our calculations predict the ³B_{2u} nearly degenerate with ¹B_{3u}, and thus the mechanism



where the intersystem coupling is through τ_z(*b*_{1g}).

4.3.2. Pyrimidine (1,3-diazine)

The calculated spectrum of pyrimidine is found in Table 9 along with the observed value for the lowest transition. The estimated ν_{max} value of ~32,000 cm⁻¹ is again in accord

Table 9. Pyrimidine

Observed			Calculated		
Symmetry	Type	Energy (cm ⁻¹)	Symmetry	Type _c	Energy (cm ⁻¹)
	<i>n</i> -π*	28,300 ^a ~32,000 ^b	³ B ₁	<i>n</i> -π*	31,721
			³ A ₁	<i>n</i> -π*	36,890
			³ A ₂	π-π*	37,342
			³ B ₂	π-π*	39,661
			³ A ₂	<i>n</i> -π*	44,338
			³ A ₁	π-π*	45,551
			³ B ₁	<i>n</i> -π*	51,645
			³ B ₂	π-π*	54,025

^a Ref. [40]. ν_{00} value. ^b Estimated ν_{\max} value.

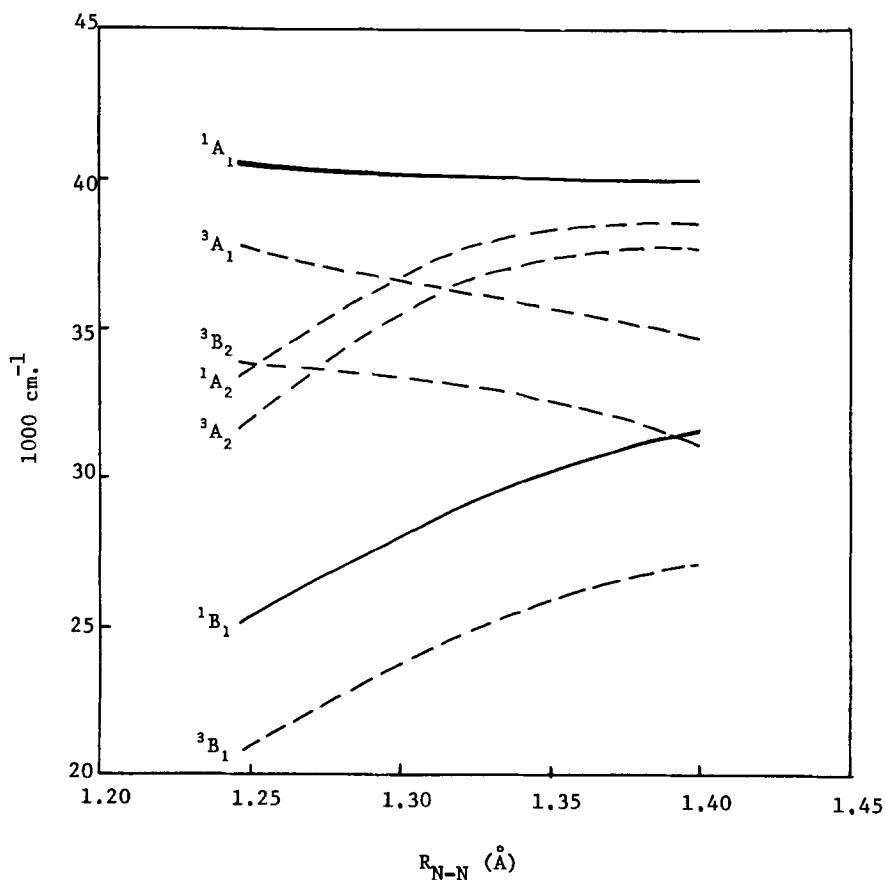


Fig. 3. Sensitivity of the calculated spectrum of pyridazine to N-N distance. Heavier lines are used to designate greater intensity: dashed lines represent forbidden states

with the calculated value of $31,721 \text{ cm}^{-1}$. Pyrimidine is the only diazine to have two calculated $n-\pi^*$ triplet states below the first $\pi-\pi^*$ triplet. Only the first of these, however, lies below the first calculated singlet, $^1B_1(n-\pi^*)$ estimated at $33,026 \text{ cm}^{-1}$ and observed at $31,073 \text{ cm}^{-1}$ [13].

4.3.3. Pyridazine (1,2-diazine)

The geometry of pyridazine is somewhat uncertain, and we have varied the geometry to test the sensitivity of the calculated spectrum to such changes. We have chosen that geometry that gives a calculated singlet spectrum in best accord with experiment. As shown in Fig. 3, the calculated transition energies are quite sensitive to the N-N bond length. It is gratifying to note that the best agreement with experiment comes from a choice of N-N bond distance of $R = 1.32 \text{ \AA}$, which is in good accord with the N-N length of 1.321 \AA found in *s*-tetrazine [41].

Table 10 contains a summary of the information available on the triplet spectrum of pyridazine. Our calculated value appears in good agreement with that from the analysis of Innes, Tincher and Pearson [42]. We find no evidence of a low-lying singlet transition such as that suggested by Cohen and Goodman [40] to explain a deactivation of the lowest triplet state leading to lack of phosphorescence. The lowest singlet, 1B_1 , is calculated to lie $4,300 \text{ cm}^{-1}$ above the lowest triplet². We might attribute the lack of observed phosphorescence to the very low energy of the first triplet which could lead to intersystem crossing directly into the ground state through $\tau_y(b_1)$.

5. Conclusions

A simple modification of the INDO/S scheme for calculating singlet excited states has been introduced and found to accurately yield the energies of triplet states. Although the change in the distance dependence of the Coulomb integrals required for the successful calculation of triplets from that used for singlets can be rationalized on theoretical grounds, the reason for an increased resonance integral for $\pi-\pi$ interactions is not clear.

The calculation of low lying triplets has been found in general to be more sensitive to the inclusion of higher lying configurations in the configuration interaction treatment than the corresponding singlets. If all pi symmetry molecular orbitals, the highest three or four sigma occupied orbitals, and two or three of the lowest-lying empty sigma orbitals are used to generate configurations, the calculated results are quite respectable, generally within $\pm 800 \text{ cm}^{-1}$ of observed band maxima. For molecules the size of benzene or greater, we have found that configurations of the $\sigma-\sigma^*$ type can be dropped from consideration, as they only slightly influence the $\pi-\pi^*$ states, and generally are calculated to lie at higher energies than experimental observations.

Calculations on pyridine and the diazines reported here agree very well with the observations to date, and suggest symmetry assignments as well as rationale for observed fluorescence and phosphorescence.

² Due to the changed geometry, the values from Ref. 13 for the singlet states of pyridazine have changed. The calculation yields $^1B_1(n-\pi^*)$ at $28,941 (0.02)$, $^1A_2(n-\pi^*)$ at $37,680 (0)$, $^1A_1(\pi-\pi^*)$ at $40,138 (0.056)$, $^1A_2(\pi-\pi^*)$ at $44,696 (0)$, $^1B_2(\pi-\pi^*)$ at $50,313 (0.04)$, $^1B_1(n-\pi^*)$ at $51,118 (0.01)$, $^1B_2(\pi-\pi^*)$ at $55,693 (0.883)$, and $^1A_1(\pi-\pi^*)$ at $57,421 (0.800)$, where the values in parentheses are calculated oscillator strengths.

Table 10. Pyridazine

Observed			Calculated		
Symmetry	Type	Energy (cm ⁻¹)	Symmetry	Type	Energy (cm ⁻¹)
	<i>n</i> - π^*	22,500 ^a	³ B ₁	<i>n</i> - π^*	24,674
			³ B ₂	π - π^*	33,105
			³ A ₁	π - π^*	36,240
			³ A ₂	<i>n</i> - π^*	36,581
			³ B ₂	π - π^*	42,043
			³ A ₂	<i>n</i> - π^*	46,996
			³ A ₁	π - π^*	50,008
			³ B ₁	<i>n</i> - π^*	54,121

^a Ref. [42]. ν_{00} value. ν_{\max} value may be ~ 2000 – 4000 cm⁻¹ higher in energy; see also L. Goodman, *J. Mol. Spectry.* **6**, 109 (1961).

We have made use of the sensitivity of the spectrum of pyridazine to its assumed geometry to estimate R_{NN} at 1.32 Å. Although we have not examined this avenue of obtaining geometries in detail, in those cases we have examined (see also Ref. 17) the geometry obtained by “fitting” spectra is very reasonable indeed.

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