

CNDO CI Calculations on Second-Row Molecules

I. Phosphorin and Thiophen

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The CNDO/S method is extended to second-row molecules and parametrized for phosphorus and sulphur. Both *sp* and *spd* basis sets are considered. The method is applied to the aromatic molecules phosphorin and thiophen. The *uv* transitions, ionization potentials and dipole moments of these molecules are satisfactorily explained.

Key words: Second-Row Molecules – Phosphorin – Thiophen

1. Introduction

In recent years a modified CNDO method (CNDO/S) has been developed by Del Bene and Jaffé [1–4] and used to calculate the electronic spectra of hydrocarbons and heterocycles. The original CNDO/S method was restricted to molecules containing, except for chlorine [4], first-row elements only. Recently, extensions to heterocycles containing sulphur atoms have been reported [5, 6].

Although SCF ground state properties (except for multipole moments, polarizabilities and inversion barriers where often even for first-row molecules extended basis sets including *3d* AOs are needed), namely the total energy, orbital energies, or atomic orbital populations, seem to be little influenced by including *3d* AOs [7], the situation for excited states might be markedly different because, in that case, singly excited configurations involving excitations to *3d* AOs lie close in energy to low lying excited valence states. For this reason we tried to extend the CNDO/S method to second-row molecules both with (*spd* basis set) and without (*sp* basis set) inclusion of *3d* AOs on second-row elements. As standard molecules to parametrize phosphorus and sulphur we used the aromatic molecules phosphorin (phosphabenzene) (1) and thiophen (2)



1



2

2. Method of Calculation

The elements of the CNDO/2 energy matrix are [8]:

$$F_{\mu\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) + [(P_{AA} - Z_A) - \frac{1}{2}(P_{\mu\mu} - 1)] \cdot \gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B) \cdot \gamma_{AB}, \quad (1)$$

$$F_{\mu\nu} = \frac{1}{2}(\beta_A^0 + \beta_B^0) \cdot S_{\mu\nu} - \frac{1}{2}P_{\mu\nu} \cdot \gamma_{AB}, \quad (2)$$

where μ and ν refer to two valence atomic orbitals (AOs) ϕ_{μ} and ϕ_{ν} . I_{μ} and A_{μ} are the ionization potential and electron affinity of ϕ_{μ} . $P_{\mu\mu}$ and $P_{\mu\nu}$ are elements of the charge density matrix (number of electrons which populate ϕ_{μ} and the overlap region $\phi_{\mu}\phi_{\nu}$, respectively) and $S_{\mu\nu}$ elements of the overlap matrix. P_{AA} (P_{BB}) refers to the total number of valence electrons on atom A (B) [found by summing all $P_{\mu\mu}$ on atom A (B)] and Z_A (Z_B) to the total number of valence electrons contributed by atom A (B). γ_{AB} (γ_{AA}) denotes the repulsion integrals between two electrons, one on atom A and the other on atom B (both on atom A). β_A^0 (β_B^0) is an adjustable parameter of atom A (B).

To avoid the exaggerated mixing of σ and π MOs (and thus the exaggerated intermingling of σ and π electronic transitions) occurring within the original CNDO/2 method, Del Bene and Jaffé found it necessary to add a further adjustable parameter which may be introduced as follows: Within the framework of the CNDO/2 programme $S_{\mu\nu}$ is calculated with respect to a standard diatomic coordinate system (the molecule is rotated such that both atoms A and B bearing ϕ_{μ} and ϕ_{ν} , respectively lie on the z axis), which means that ϕ_{μ} and ϕ_{ν} referred to the molecular coordinate system are expanded (with expansion coefficients $a_{\mu i}$ and $a_{\nu j}$) into the new set $\{\varphi_i\}$ referred to the diatomic coordinate system, i.e.:

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle = \sum_i \sum_j a_{\mu i} a_{\nu j} \langle \varphi_i | \varphi_j \rangle = \sum_i \sum_j a_{\mu i} a_{\nu j} S_{ij}. \quad (3)$$

By multiplying any of the S_{ij} integrals in (3) by any arbitrary constant K_{ij} we arrive at modified integrals $S'_{\mu\nu}$ without destroying their rotational invariance:

$$S'_{\mu\nu} = \sum_i \sum_j a_{\mu i} a_{\nu j} S_{ij} K_{ij} = \sum_i \sum_j a_{\mu i} a_{\nu j} S'_{ij}. \quad (4)$$

On replacing $S_{\mu\nu}$ in (2) by $S'_{\mu\nu}$ of (4) we obtain modified off-diagonal energy matrix elements which are still rotationally invariant.

Del Bene and Jaffé retained in their study of first-row molecules, as in the original CNDO/2 method, $K_{ij} = 1$ except for i and j referring to p_{π} AOs where they empirically derived $K_{ij} = K_p = 0.585$. In the present study of second-row molecules we found it, in addition, necessary to introduce a similar correction to the off-diagonal matrix elements (2) whenever i or j of (4) refers to a $3d$ AO. As is well known, the original CNDO/2 method (spd basis set) predicts, due to exaggerated $3d$ participation (the CNDO/2 method with sp basis yields the correct sequence) the wrong MO sequence $a_{2\pi}$, $a_{1\sigma}(n)$, $b_{1\pi}$ [7, 9] for the three highest occupied MOs of thiophen while from photoelectron spectroscopy the two

upper orbitals are known to be $a_{2\pi}$, $b_{1\pi}$ [10]. Furthermore, in the present study, we found it impossible to predict the correct sequence of $\sigma(n)\pi^*$ and $\pi\pi^*$ states in phosphorin without including the aforementioned $3d$ AO correction. Both difficulties were overcome by choosing K_{ij} (i or $j = 3d$ AO) $= K_d = 0.300$. This value was assigned by an independent variation of both K_d and β_p^0 (see below) in the case of the phosphorin molecule.

Selection of Core and Repulsion Parameters

The values of the remaining parameters of (1) and (2) were chosen as follows: For the orbital electronegativities $\frac{1}{2}(I_\mu + A_\mu)$ we used both the values of Pople, Santry, and Segal (PSS) [8, 11–14] of the original CNDO/2 scheme and the values due to Hinze and Jaffé [15] which were also used in the second CNDO/S parametrization by Del Bene and Jaffé (DBJ2) [3]. The one-center repulsion integrals are derived from $\gamma_{AA} = I_\mu - A_\mu$, where s AO (μ refers to s AOs) and p AO (μ refers to p AOs) data are taken into account with the PSS and DBJ2 parametrizations, respectively. While these values are very similar for first-row atoms, the PSS values are significantly lower than the DBJ2 ones, for second-row atoms. Since the latter values are more close to values used in the Pariser, Parr, and Pople (PPP) calculations [16, 17] we tried a third parametrization (called PSS2 to keep it distinct from the former PSS, now called PSS1 parametrization) making use of PSS1 $\frac{1}{2}(I_\mu + A_\mu)$ core and DBJ2 repulsion parameters. It should be noted that, for first-row molecules, these different sets of parameters (PSS1, PSS2, and DBJ2) lead to nearly identical results. In all cases the two-center repulsion integrals γ_{AB} were computed from the Nishimoto-Mataga formula [18].

Based on the orbital energies and orbitals obtained from the modified CNDO SCF method described above a configuration interaction (CI) calculation involving the 50 lowest singly excited configurations was performed. For each of distinct parameter sets (PSS1, PSS2, and DBJ2) the bonding parameter β_A^0 ($A = P$ and S) was optimized with regard to the CI transition energies. As mentioned above, β_p^0 was determined by simultaneously and independently optimizing K_d . The values thus obtained together with the orbital electronegativity and electron repulsion parameters are gathered in Table 1.

The modifications of the CNDO/2 method described above were introduced into the standard CNDO/INDO programme (QCPE 141, available from the Quantum Chemistry Program Exchange, Bloomington, Indiana). The CI subroutines were taken from the CNDO/S programme (QCPE 174) and, by taking account of Brillouin's theorem [19], simplified in order to save computer time.

3. Numerical Results

Phosphorin

Structural data of phosphorin are known from X-ray measurements on 2,6-di-methyl-4-phenylphosphorin [20] and microwave data for phosphorin [21]. The parameters used in the present study are: symmetry = C_{2v} ; bond

Table 1. Parameters used in the extended CNDO/S method

Atom	Orbital electronegativities $\frac{1}{2}(J_{\mu} + A_{\mu})$ (eV)				Repulsion integral γ_{AA} (eV)			
	<i>s</i>		<i>p</i>		<i>d</i>		<i>p</i>	
	PSS1/PSS2	DBJ2	PSS1/PSS2	DBJ2	PSS1/PSS2	DBJ2	PSS1	PSS2/DBJ2
H	7.176	7.176					12.85	12.85
C	14.051	14.96	5.572	5.805			10.778	10.93
P	14.0327	14.34	5.4638	7.235	0.5	0.0 ^a	7.142	10.51
S	17.6496	15.81	6.989	8.41	0.713	0.0 ^a	7.3542	9.82
	$-\beta_{\lambda}^0/spd$ (eV)				$-\beta_{\lambda}^0/sp$ (eV)			
	PSS1	PSS2	DBJ2	PSS1	PSS2	DBJ2		
H	12.0 ^b	12.0 ^b	12.0 ^b	12.0 ^b	12.0 ^b	12.0 ^b	$K_p = 0.585$	
C	17.5 ^b	17.5 ^b	17.5 ^b	17.5 ^b	17.5 ^b	17.5 ^b	$K_d = 0.300$	
P	25.0	22.0	20.0	18.0	17.0	16.5		
S	22.0	23.0	20.0	20.0	16.0	16.0		

^a Assumed to be zero.^b Values derived by Del Bene and Jaffé [3].

lengths: P-C = 1.74 Å, C-C = 1.40 Å, C-H = 1.083 Å; bond angles: C₆P₁C₂ = 103°, P₁C₂C₃ = 123°, C₂C₃C₄ = 124°, C₃C₄C₅ = 123°.

Previous CNDO/2 calculations by Oehling and Schweig [22] on phosphorin revealed the sequence $a_{2\pi}$, $b_{1\pi}$ for the two highest occupied π MOs. Thus this sequence is reversed relative to pyridine. The prediction of sequence reversal was confirmed by means of the photoelectron spectrum of 2,4,6-tri-tert-butyl-phosphorin by Oehling, Schäfer, and Schweig [23] and subsequently for phosphorin by Batich, Heilbronner, Hornung, Ashe, Clark, Cobley, Kilcast, and Scanlan in agreement with STO-3 G calculations including 3d AOs on the phosphorus atom [24]. uv data (λ_{\max} values and molar extinction coefficients) have been reported by Ashe [25] and the dipole moment by Kuczkowski and Ashe [21].

Table 2 summarizes the calculated and experimental values of the uv transition energies, oscillator strengths (experimental values refer to ϵ_{\max} , the molar extinction coefficient), ionization potentials (based on Koopmans' theorem [26]) and dipole moment. As the comparison reveals, the agreement between theoretical and measured values is surprisingly good. Except for the DBJ2 results we get always the correct orbital sequence $a_{2\pi}$, $b_{1\pi}$, $a_{1\sigma}$. The computed dipole moments are somewhat too high. The main contribution arises from the phosphorus lone pair, not from the net atomic charges. Again the DBJ2 result are strikingly poor. All calculations performed predict the same state sequence ${}^1B_1(n\pi^*)$, ${}^1B_2(\pi\pi^*)$, ${}^1A_1(\pi\pi^*)$ for the first three observed uv bands. Accordingly, phosphorin has a spectrum analogous to pyridine [1, 3]. Thus the energy change due to the reversal of the upper π MOs of phosphorin relative to pyridine is over-compensated by the influence of the two electron integrals involved in the calculation of the transition energies. Interestingly, this reversal occurs before CI, but is strengthened by CI. With regard to solution data [25], the ${}^1B_1(n\pi^*)$ and ${}^1A_1(\pi\pi^*)$ states are shifted to lower energies when compared to pyridine while the ${}^1B_2(\pi\pi^*)$ state remains nearly at the same energy.

The PSS1 and PSS2 parametrizations produce nearly the same results which are, however, different from the DBJ2 results. This result suggests that repulsion parameters have less influence on semiempirical SCF calculations than core parameters (orbital electronegativities) have. PSS core parameters [11-14] seem to give better results for second-row molecules than those due to Hinze and Jaffé [15]. Only low 3d AO populations are found (in the range of 0.1-0.2). Nevertheless the calculations with inclusion of 3d AOs produce appreciably better dipole moments. The influence of 3d AOs on the state energies seem to be unessential. Useful spectral result can equally well be obtained with a sp basis set. However, this result can not be generalized. Calculations on other phosphorus compounds showed that there are cases where, only with inclusion of 3d AOs, reasonable results are obtained [27].

Thiophen

Thiophen has been investigated more thoroughly than any other organic sulphur compound with respect to possible effects arising from the 3d AOs on the sulphur atom. Such effects were first quantitatively considered by Bielefeld

Table 2. Calculated and experimental *uv*-transition energies, intensities, ionization potentials and dipole moments for phosphorin
Symmetries (transitions), state energies^a (eV) (oscillator strengths^b)

Observed ^{c,d} [25]	Calculated		Symmetries (transitions), state energies ^a (eV) (oscillator strengths ^b)					
	PSS1/spd	PSS2/spd	DBJ2/spd	DBJ2/sp				
4.3(250)	${}^1B_1(n\pi^*)$ 4.4(0)	${}^1B_1(n\pi^*)$ 4.4(0)	${}^1B_1(n\pi^*)$ 4.4(0)	${}^1B_1(n\pi^*)$ 4.4(0)				
5.0(8500)	${}^1B_2(\pi\pi^*)$ 4.7(0.02)	${}^1B_2(\pi\pi^*)$ 4.7(0.01)	${}^1B_2(\pi\pi^*)$ 4.8(0.03)	${}^1B_2(\pi\pi^*)$ 4.7(0.03)				
	${}^1A_2(n\pi^*)$ 4.9(0)	${}^1A_2(n\pi^*)$ 5.7(0)	${}^1A_1(\pi\pi^*)$ 5.8(0.06)	${}^1A_2(n\pi^*)$ 5.7(0)				
5.8(19000)	${}^1A_1(\pi\pi^*)$ 5.7(0.04)	${}^1A_1(\pi\pi^*)$ 5.8(0.03)	${}^1A_3(n\pi^*)$ 5.9(0)	${}^1A_1(\pi\pi^*)$ 5.8(0.2)				
	${}^1B_1(\sigma\pi^*)$ 6.3(0)	${}^1B_1(\sigma\pi^*)$ 6.4(0)	${}^1A_3(\sigma\pi^*)$ 6.1(0)	${}^1A_2(\sigma\pi^*)$ 6.2(0)				
	${}^1B_2(\pi\pi^*)$ 6.5(0.6)	${}^1B_2(\pi\pi^*)$ 6.5(0.8)	${}^1B_3(\sigma\pi^*)$ 6.5(0)	${}^1B_1(\sigma\pi^*)$ 6.6(0)				
	${}^1A_1(\pi\pi^*)$ 6.5(0.9)	${}^1A_2(\sigma\pi^*)$ 6.6(0)	${}^1B_2(\pi\pi^*)$ 6.6(0.9)	${}^1A_1(\pi\pi^*)$ 6.6(0.9)				
	${}^1A_2(\sigma\pi^*)$ 6.9(0)	${}^1A_1(\pi\pi^*)$ 6.7(1.0)	${}^1A_3(\pi\pi^*)$ 6.7(1.0)	${}^1B_2(\pi\pi^*)$ 6.7(0.9)				
Ionization potentials ^c (eV)								
Observed ^c [24]	Assignment [23, 24]	<i>Ab initio</i> ^e [24]	PSS1/spd	PSS2/spd	PSS1/sp	PSS2/sp	DBJ2/spd	DBJ2/sp
9.2	$b_{1\pi}$	6.2	9.6	9.7	10.3	9.4	9.6	10.3
9.8	$a_{2\pi}$	7.2	10.0	10.0	10.1	9.7	9.7	10.0
10.0	$a_{1\sigma}(n)$	8.0	10.2	11.3	11.7	10.4	11.2	11.6
Dipole moment (D)								
Observed [21]	PSS1/spd	PSS2/spd	DBJ2/spd	PSS1/sp	PSS2/sp	DBJ2/sp		
1.54	2.49	2.41	3.84	3.17	3.54	4.84		

^a Observed states and calculated states which correspond to observed states are underlined.

^b The oscillator strength were calculated with determinantal wavefunctions. The one- and two-center off-diagonal matrix elements of the dipole operator [3] were, in agreement with the original programme, neglected.

^c Observed values were rounded off.

^d Oscillator strengths are not known. The values given refer to the molar extinction coefficient ($1 \text{ Mol}^{-1} \text{ cm}^{-1}$).

^e The calculated values are based on Koopman's theorem [26].

and Fitts [28] within the PPP-method and then by Clark [9] using the CNDO/2 procedure. *Ab initio* studies have been reported by Clark [29] and Gelius, Roos, and Siegbahn [30]. A CI study, however, without inclusion of $3d$ AOs, and using a procedure rather similar to the INDO method [8] has already been published (Yonezawa, Konishi, and Kato [31]).

The structural parameters used in the present study and derived from microwave data [32, 33] are: symmetry = C_{2v} ; bond lengths: $S_1-C_2 = 1.718 \text{ \AA}$, $C_2-C_3 = 1.352 \text{ \AA}$, $C_3-C_4 = 1.455 \text{ \AA}$; bond angles: $C_5S_1C_2 = 91^\circ 12'$, $S_1C_2C_3 = 112^\circ 36'$, $C_2C_3C_4 = 111^\circ 48'$. For all C-H bond lengths the standard value of 1.083 \AA was used. The ionization potentials have been measured by photoelectron spectroscopy [10]. Both the vapor (Price and Walsh [34], Milazzo [35-37]) and solution (isooctane: Boig, Costa, and Osvar [38], hexane: Leandri, Mangini, Montanari, and Passerini [39], hexane: Sicé [40]) *uv* spectra are accessible. Moreover, a low lying triplet state has been observed (Padhye and Desai [41]).

Table 3 lists and compares the computed transition energies, oscillator strengths, ionization potentials, and dipole moments with experimental data. The agreement between theoretical and measured quantities is satisfactory. The third ionization potential was assigned to ionization from the $b_{1\pi}$ MO [10]. This experimental assignment is at variance with *ab initio* [29, 30] and semi-empirical [9, 31] work (based on Koopmans' theorem [26]). In accord with this work, the present calculations, too, predict the third ionization potential to correspond to the $a_{1\sigma}$ MO. The interpretation of the *uv*-spectrum of thiophen is more complicated than in the case of phosphorin. All calculations agree that there is no low lying ${}^1B_1(n\pi^*)$ state, a result which is equally valid for furan [2]. The state sequence for furan was predicted to be ${}^1B_2, {}^1A_1, {}^1A_1, {}^1B_2$. The DBJ2 and all *sp* parametrizations yield, in agreement with the preceding all-valence-electron calculation of Yonezawa, Konishi, and Kato [31], the same sequence of observed states. However, in these cases (DBJ2 and all *sp* parametrization) we were not able to fit all four bands equally well. The second 1A_1 and 1B_2 states are always calculated to be 1-2 eV too high.

While the inclusion of the $3d$ AOs on sulphur produces only negligible effects on the ground state of thiophen a strong influence on the excited states is observed. Following the $b_{1\pi}$ and $a_{2\pi}$ virtual orbitals there are five virtual orbitals which are nearly pure d AOs. The interaction of the corresponding configurations with the valence transition configurations reorders the state sequence within the PSS1/*spd* and PSS2/*spd* parametrizations to ${}^1A_1, {}^1B_2, {}^1B_2, {}^1A_1$. A similar effect has been reported by Bielefeld and Fitts [28] when they included $3d$ and $4p_z$ AOs in the basis set of a PPP treatment.

The question about the correct state sequence (${}^1B_2, {}^1A_1, {}^1A_1, {}^1B_2$ or ${}^1A_1, {}^1B_2, {}^1B_2, {}^1A_1$) of thiophen is difficult to answer at present. Compared with the spectrum of furan the whole thiophen spectrum is shifted to longer wavelengths, especially the first 1A_1 band, so that the first 1B_2 and 1A_1 bands are only separated by 0.1 eV (furan = 0.6 eV, cf. [2]). Then follow two well separated bands at 5.6 and 6.6 eV. Since the first two bands strongly overlap nothing can be gained from intensity considerations. The third band, however, is reported to be weak and the next one to be strong [10, 34-37]. This result clearly favours the

Table 3. Calculated and experimental np -transition energies, intensities, ionization potentials and dipole moment for thiophen
Symmetries (transitions), state energies^a (eV) (oscillator strengths^b)

Observed ^{c,d} [34–37, 40]	Calculated	PSS 1/spd	PSS 2/spd	DBJ 2/spd	PSS 1/sp	PSS 2/sp	DBJ 2/sp
5.2	${}^1B_2(\pi\pi^*)$ 5.5(0.2)	${}^1A_1(\pi\pi^*)$ 5.0(0.1)	${}^1A_1(\pi\pi^*)$ 5.4(0.06)	${}^1B_2(\pi\pi^*)$ 5.4(0.3)	${}^1B_2(\pi\pi^*)$ 5.4(0.2)	${}^1B_2(\pi\pi^*)$ 5.1(0.2)	${}^1B_2(\pi\pi^*)$ 5.2(0.2)
5.3	${}^1A_1(\pi\pi^*)$ 6.0(0.2)	${}^1B_2(\pi\pi^*)$ 5.4(0.2)	${}^1B_2(\pi\pi^*)$ 5.5(0.3)	${}^1A_1(\pi\pi^*)$ 5.8(0.02)	${}^1A_1(\pi\pi^*)$ 5.5(0.1)	${}^1A_1(\pi\pi^*)$ 5.6(0.03)	${}^1A_1(\pi\pi^*)$ 5.9(0.08)
	${}^1A_1(\pi\pi^*)$ 7.7(1.0)	${}^1A_2(\pi\sigma^*)$ 5.8(0)	${}^1A_2(\pi\sigma^*)$ 6.0(0)	${}^1B_1(\pi\sigma^*)$ 6.8(0)	${}^1B_1(n\pi^*)$ 6.7(0)	${}^1B_1(n\pi^*)$ 6.5(0)	${}^1B_1(\pi\sigma^*)$ 6.4(0)
	${}^1B_2(\pi\pi^*)$ 7.9(0.4)	${}^1B_1(\pi\sigma^*)$ 6.1(0)	${}^1B_1(\pi\sigma^*)$ 6.2(0)	${}^1B_1(n\pi^*)$ 7.0(0)	${}^1A_1(\pi\pi^*)$ 6.9(0.6)	${}^1B_1(\pi\sigma^*)$ 7.0(0)	${}^1B_1(n\pi^*)$ 6.9(0)
5.6 (weak)		${}^1B_2(\pi\pi^*)$ 6.2(0.08)	${}^1B_1(\pi\sigma^*)$ 6.6(0)	${}^1A_1(\pi\pi^*)$ 7.3(0.7)	${}^1B_2(\pi\pi^*)$ 7.1(0.08)	${}^1A_1(\pi\pi^*)$ 7.1(0.6)	${}^1A_2(\pi\sigma^*)$ 6.9(0)
		${}^1B_1(n\pi^*)$ 6.5(0)	${}^1B_1(n\pi^*)$ 6.7(0)	${}^1A_2(n\sigma^*)$ 7.3(0)	${}^1A_2(\pi\sigma^*)$ 7.2(0)	${}^1A_2(\pi\sigma^*)$ 7.2(0)	${}^1A_1(\pi\pi^*)$ 7.2(0.6)
		${}^1B_1(\pi\sigma^*)$ 6.7(0)	${}^1B_2(\pi\pi^*)$ 6.8(0.08)	${}^1B_1(\sigma\pi^*)$ 7.6(0)	${}^1A_2(\sigma\pi^*)$ 7.3(0)	${}^1A_2(\sigma\pi^*)$ 7.3(0)	${}^1B_1(\sigma\pi^*)$ 7.5(0)
6.6 (strong)		${}^1A_1(\pi\pi^*)$ 6.7(0.4)	${}^1A_1(\pi\pi^*)$ 7.1(0.6)	${}^1B_1(\sigma\pi^*)$ 7.7(0)	${}^1B_2(\pi\pi^*)$ 7.6(0.04)	${}^1B_2(\pi\pi^*)$ 7.6(0.04)	${}^1A_2(\sigma\pi^*)$ 7.6(0)
				${}^1B_2(\pi\pi^*)$ 7.7(0.06)			${}^1B_2(\pi\pi^*)$ 7.8(0)
							${}^1B_2(\pi\pi^*)$ 8.0(0.03)

Ionization potentials^f (eV)

Observed ^e [10]	Assignment [10, 30]	<i>Ab initio</i> ^o [30]	PSS 1/spd	PSS 2/spd	DBJ 2/spd	PSS 1/sp	PSS 2/sp	DBJ 2/sp
8.9	$a_{2\pi}$	9.0	9.3	9.3	9.5	9.1	9.2	9.4
9.5	$b_{1\pi}$	9.3	9.6	10.2	10.9	9.7	10.4	10.0
12.1	$a_{1\sigma}(n)/b_{1\pi}^*$	12.9	12.2	12.7	13.1	12.2	12.5	13.0

Dipole moment (D)	<i>Ab initio</i> /spd [30]	PSS 1/spd	PSS 2/spd	DBJ 2/spd	PSS 1/sp	PSS 2/sp	DBJ 2/sp
0.60	0.61	0.96	0.93	1.13	1.14	1.88	2.65

^{a,b,c} cf. the corresponding footnotes of Table 2. ^d For the oscillator strength given, cf. Ref. [40]. ^e cf. the corresponding footnote of Table 2.

^f Transitions involving σ MOs have been omitted here because the corresponding transition energies were not obtained by a CI calculation.

^g The assignment of the third ionization potential to the $b_{1\pi}$ MO [10] has been questioned by Gelius, Roos and Siegbahn [30] who favour an assignment to the $a_{1\sigma}(n)$ MO.

PSS 1/*spd* and PSS 2/*spd* assignments of the second 1B_2 and 1A_1 states. Moreover, the transition energies are most satisfactorily reproduced by the PSS 1/*spd* parametrization.

All parametrizations yield low lying triplet states ($^3B_2(\pi\pi^*) = 2.4$ eV, $^3A_1(\pi\pi^*) = 3.4$ eV in the case of the PSS 1/*spd* parametrization; experimentally, by direct absorption, a triplet state at 3.9 eV has been seen [41]). This result is somewhat surprising in view of the fact that the first triplet states for pyridine ($^3A_1(\pi\pi^*) = 3.3$ eV/DBJ2 parametrization; experimental value = 3.7 eV [42]) and phosphorin ($^3A_1(\pi\pi^*) = 3.4$ eV/PSS 1/*spd*) are reproduced quite well. However, it is interesting to note that also for furan a low lying first triplet state ($^3B_2(\pi\pi^*) = 2.3$ eV, second triplet state: $^3A_1(\pi\pi^*) = 3.4$ eV) is predicted.

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References

1. Del Bene, J., Jaffé, H.H.: J. Chem. Phys. **48**, 1807 (1968)
2. Del Bene, J., Jaffé, H.H.: J. Chem. Phys. **48**, 4050 (1968)
3. Ellis, R.L., Kuehnlenz, G., Jaffé, H.H.: Theoret. Chim. Acta (Berl.) **26**, 131 (1972)
4. Kuehnlenz, G., Jaffé, H.H.: J. Chem. Phys. **58**, 2238 (1973)
5. Pfister-Guillouzo, G., Gonbeau, D., Deschamp, J.: J. Mol. Struct. **14**, 81 (1972)
6. Kroner, J., Proch, D.: Tetrahedron Letters 2537 (1972)
7. See, for example: Clark, D.T.: Organic compounds of sulphur, selenium, and tellurium, Specialist Periodical Reports. London: The Chemical Society, Burlington House 1970
8. Pople, J.A., Beveridge, D.L.: Approximate molecular orbital theory. New York: McGraw Hill 1970
9. Clark, D.T.: Tetrahedron **24**, 2663 (1968)
10. Derrik, P.J., Asbrink, L., Edquist, O., Jonsson, B.O., Lindholm, E.: Int. J. Mass Spectrometr. Ion Phys. **6**, 177 (1971)
11. Pople, J.A., Santry, D.P., Segal, G.A.: J. Chem. Phys. **43**, 129 (1965)
12. Pople, J.A., Segal, G.A.: J. Chem. Phys. **43**, 136 (1965)
13. Pople, J.A., Segal, G.A.: J. Chem. Phys. **44**, 3289 (1966)
14. Santry, D.P., Segal, G.A.: J. Chem. Phys. **47**, 158 (1967)
15. Hinze, J., Jaffé, H.H.: J. Am. Chem. Soc. **84**, 540 (1962)
16. Pariser, R., Parr, R.G.: J. Chem. Phys. **21**, 767 (1953)
17. See, for example: Johnstone, R.A.W., Ward, S.D.: Tetrahedron **25**, 5485 (1969)
18. Nishimoto, K., Mataga, N.: Z. Physik. Chem. **12**, 335 (1957)
19. Brillouin, L.: Les champs self consistents de Hartree et de Fock. Paris: Hermann et Cie 1934
20. Bart, J.C.J., Daly, J.J.: Angew. Chem. **80**, 843 (1968)
21. Kuczkowski, R.L., Ashe, A.J.: J. Mol. Spectr. **42**, 457 (1972)
22. Oehling, H., Schweig, A.: Tetrahedron Letters 4941 (1970)
23. Oehling, H., Schäfer, W., Schweig, A.: Angew. Chem. **83**, 723 (1971); Angew. Chem. internat. Ed. **10**, 656 (1971)
24. Batich, C., Heilbronner, E., Hornung, V., Ashe, A.J., Clark, D.T., Cogley, U.T., Kilcast, D., Scanlan, I.: J. Am. Chem. Soc. **95**, 928 (1973)
25. Ashe, A.J.: J. Am. Chem. Soc. **93**, 3293 (1971)
26. Koopmans, T.: Physica **1**, 104 (1934)
27. Schulte, K.W., Schweig, A.: unpublished results
28. Bielefeld, M.J., Fitts, D.D.: J. Am. Chem. Soc. **88**, 4804 (1966)
29. Clark, D.T., Armstrong, D.R.: Chem. Commun. 319 (1970)
30. Gelius, U., Roos, B., Siegbahn, P.: Theoret. Chim. Acta (Berl.) **27**, 171 (1972)

31. Yonezawa, T., Konishi, H., Kato, H.: *Bull. Chem. Soc. Japan* **42**, 933 (1969)
32. Bak, B., Christensen, D., Hansen-Nygaard, L., Rastrup-Andersen, J.: *J. Mol. Spectr.* **7**, 56 (1961)
33. Bak, B., Christensen, D., Rastrup-Andersen, J., Tannenbaum, E.: *J. Chem. Phys.* **25**, 892 (1956)
34. Price, W.C., Walsh, A.D.: *Proc. Roy. Soc. (Lond.) A* **179**, 201 (1941)
35. Milazzo, G.: *Spectrochim. Acta* **2**, 245 (1944)
36. Milazzo, G.: *Gazz. Chim. Ital.* **78**, 835 (1948)
37. Milazzo, G.: *Gazz. Chim. Ital.* **83**, 392 (1953)
38. Boig, F.S., Costa, G.W., Osvar, I.: *J. Org. Chem.* **18**, 775 (1953)
39. Leandri, G., Mangini, A., Montanari, F., Passerini, R.: *Gazz. Chim. Ital.* **85**, 769 (1955)
40. Sicé, J.: *J. Phys. Chem.* **64**, 1572 (1960)
41. Padhye, M.R., Desai, S.R.: *Proc. Phys. Soc. (Lond.) A* **65**, 298 (1952)
42. Evans, D.F.: *J. Chem. Soc. (London)* 3885 (1957)

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