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Extension of the CNDO/S Method to the Calculation of Aromatic and Heterocyclic Compounds Containing Si, P, S and Cl

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The extension of the CNDO/S calculation to aromatic and heterocyclic compounds containing Si, P, S or Cl was investigated in detail. Parameters of the second-row elements were optimized by using as many types of compound as possible. The *spd* basis sets were shown to be superior to the *sp* basis sets in the calculation. The results of this investigation showed that not only calculated transition energies but also orbital energies coincide very well with observed values without exception.

The method presented in this work is expected to be widely applicable to the calculation of the electronic states of many aromatic and heterocyclic compounds containing second-row elements.

Keywords——CNDO/S; *spd* basis set; transition energy; ionization potential; dipole moment; silicon-containing compound; phosphorus-containing compound; sulfur-containing compound; chlorine-containing compound

The semi-empirical CNDO/S method, developed by Jaffé *et al.*,[1,2] is useful for theoretical investigations on the electronic states of organic compounds. The usefulness of this method for organic chemists, however, is limited at present to the calculation of compounds containing only the first-row elements, because the selections of both the basis sets and the parameters of second-row elements have not yet been well established.

The purpose of the present investigation was firstly to select parameters for silicon(Si), phosphorus(P), sulfur(S) and chlorine(Cl) atoms adequate for calculations of various types of aromatic and heterocyclic compounds, and secondly to decide whether the *spd* or the *sp* basis set is superior in such calculations. Here, the type of a compound means the type of chemical structure of the moiety surrounding the second-row element.

Experimental

Method of Calculation——The elements of the Fock matrix are written in the CNDO/S method[1] as

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + [(P_{\mathrm{AA}} + Z_{\mathrm{A}}) - \frac{1}{2}(P_{\mu\mu} - 1)]\gamma_{\mathrm{AA}}$$
$$\sum_{\mathrm{B}\neq\mathrm{A}} (P_{\mathrm{BB}} - Z_{\mathrm{B}})\gamma_{\mathrm{AB}} \qquad (1)$$

$$F_{\mu\nu}=\frac{1}{2}(\beta^0_{\mathrm{A}}+\beta^0_{\mathrm{B}})S_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}} \qquad (2)$$

where I_μ and A_μ are the ionization potential and the electron affinity of a valence atomic orbital μ, respectively, and $-1/2(I_\mu+A_\mu)$ is the "core integral" and β^0_{A} is the "bonding parameter" of an atom A. The one-center repulsion integral, γ_{AA}, and the two-center repulsion integral, γ_{AB}, were estimated according to the Pariser formula[3a)] and the Nishimoto–Mataga formula,[3b)] respectively. The overlap integral, $S_{\mu\nu}$, between the valence atomic orbitals μ and ν was evaluated by means of Eq. 3.

$$S_{\mu\nu}=S^{\sigma}_{\mu\nu}+0.585S^{\pi}_{\mu\nu} \qquad (3)$$

When one of or both of these two orbitals are 3*d* orbitals, $S_{\mu\nu}$ was multiplied by the coefficient 0.30[4)] (Eq. 4).

$$S_{\mu\nu}=0.30S^{d}_{\mu\nu} \qquad (4)$$

The CNDO/2 program (QCPE No. 141) was modified and used in this study. All CNDO/S calculations were carried out on a FACOM M-382 computer at the Computation Center of Kyushu University.

Selection of Basis Sets and Parameters——In order to select both the basis sets and the parameters for the four elements, various types of aromatic and heterocyclic compounds containing one of the four elements for which spectral data were known were used. The names of the compounds used are given in Table I.

When transition energies are used to select the parameters of a particular element in organic molecules, it is usual to compare the calculated transition energies with the observed band energies measured in the vapor phase. Many aromatic and heterocyclic compounds, however, have fairly low vapor pressure and their electronic absorption spectra are usually measured in solvents. In fact, the absorption spectra of most of the compounds given in Table I have been measured only in solvents. Parameters were optimized, therefore, so as to give calculated transition energies which are very close to the observed values measured in non-polar solvents.

There have been several papers reporting the results of CNDO/S calculations of the transition energies of aromatic and heterocyclic compounds containing Si,[5)] P,[4)] S[4,6-9)] or Cl.[10)] In these investigations, calculations have been carried out with[4,5,7-9)] or without[4-6,9)] the inclusion of empty 3*d* orbitals of the second-row elements. A survey of these investigations indicated that the calculations using the *spd* basis sets have afforded satisfactory results without exception, but those using the *sp* basis sets have sometimes afforded unsatisfactory results. In molecular orbital calculation of organic compounds, moreover, it can be expected that when more atomic orbitals of an element are used as the basis set, better results will be obtained. In fact, in our preliminary investigation on the calculations of transition energies of several compounds containing second-row elements, it was found that the calculations using the *spd* basis set gave values very close to the observed values, but the calculations using the *sp* basis set did not give satisfactory results. In the present investigation, therefore, 3*d* orbitals were included in all calculations.

With regard to the parameters for the first-row elements, those reported by Jaffé *et al.*[2)] were used without modification, because, in our preliminary investigation on the calculations of transition energies of several aromatic and heterocyclic compounds containing first-row elements alone, it was found that the values calculated by employing their proposed parameters coincided very well with the observed values measured in non-polar solvents.

In order to select the most suitable parameters for the second-row elements, transition energies of a wide variety of S-containing compounds (VIII—XVI) were calculated at first by using two sets (A and B sets) of the core integral and the one-center repulsion integral of an atom A, γ_{AA}, and the results of calculations were compared with each other. Here, the A set is the combination of the core integral given by Santry and Segal[11a)] with the one-center

Table I. Compounds Used

No.	Compound	No.	Compound
I	Silabenzene	XII	4*H*-Thiopyran-4-one
II	Phenylsilane	XIII	4*H*-Thiopyran-4-thione
III	Trimethylphenylsilane	XIV	Methylphenylsulfoxide
IV	Phosphabenzene	XV	Methylphenylsulfone
V	Phenylphosphine	XVI	Benzenesulfonamide
VI	Dimethylphenylphosphine	XVII	Chlorobenzene
VII	1-Methylphosphole	XVIII	1,4-Dichlorobenzene
VIII	Thiophene	XIX	1,3-Dichlorobenzene
IX	Benzenethiol	XX	3-Chloropyridine
X	Methylphenylsulfide	XXI	Benzyl chloride
XI	4*H*-Pyran-4-thione		

TABLE II. Selected Parameters (eV)

Atom	Core integral			γ_{AA}	β^0_A
	s	p	d		
H	7.175			12.85	−12.0
C	14.960	5.805		10.93	−17.5
N	20.485	8.480		11.88	−26.0
O	27.255	10.965		15.13	−30.0
Si	10.033	4.133	0.337	9.866	−8.5
P	14.033	5.464	0.500	8.668	−15.0
S	17.650	6.989	0.713	6.604	−17.0
Cl	21.591	8.708	0.977	7.428	−20.0

repulsion integral derived from that core integral and Slater's 3*s* ionization potential of an atom.[12)] The B set is the combination of the core integral and the one-center repulsion integral, both derived from the ionization potential and electron affinity of an atom according to Hinze and Jaffé.[13)] In these calculations, the configuration interaction was treated by considering the lowest 60 singly excited configurations,[14)] and the atomic bonding parameter for the S atom, β^0_S, was optimized so as to give the best results. The results showed that the transition energies calculated by using the A set coincided very well with the observed values, while those calculated by using the B set did not. The superiority of the A set to the B set was assumed to hold in the Si, P and Cl compounds, and the A set was used throughout this investigation.

In the calculations of Si-, P- and Cl-containing compounds, the configuration interaction was treated in the same way as in the case of the calculations of S-containing compounds.

All of β^0_{Si}, β^0_P and β^0_{Cl} were also optimized to give the best results, and are shown in Table II together with β^0_S (already optimized), the core integrals and the one-center repulsion integrals used in this work. The Slater exponent of an orbital calculated by means of the empirical rule given by Slater[11b)] was used.

Molecular Geometries——Among the twenty-one compounds listed in Table I, the molecular geometries of only nine compounds have been established so far. Those compounds are II, IV, VIII, XI, XIII and XVII, whose molecular geometries have been determined by physico-chemical methods, and I, V and IX, whose molecular geometries have been optimized by quantum chemical calculations. With regard to the other compounds, therefore, it was necessary to assume their molecular geometries. The phenyl rings of all benzene derivatives including II, V, IX and XVII, were assumed to form a regular hexagon having C–C and C–H bond lengths of 1.397 and 1.084 Å, respectively.

The following geometries were used in this investigation. I: The geometry optimized by *ab initio* calculation[15)] was used. II: The C–Si and Si–H bond lengths were taken from the electron diffraction data.[16)] A tetrahedral Si atom was assumed and one of the three H atoms of the SiH_3 group was placed on the plane of the phenyl ring. III: The geometry of the $C_{(ar)}$–$Si(CH_3)_3$ group of III was assumed to be identical with that of the same group in 9-trimethylsilylphenanthrene, whose geometry has been established by the X-ray diffraction method.[17)] IV: The geometry established by the electron diffraction method[18)] was used. V: The C–P and P–H bond lengths and the C–P–H angle were taken from the geometry of V optimized by MINDO/3 calculation.[19)] Both of the H atoms of the PH_2 group were placed symmetrically above the plane of the phenyl ring. VI: The $C_{(ar)}$–P bond length was assumed to be identical with that of V. The P–$C_{(Me)}$ and $C_{(Me)}$–H bond lengths were assumed to be 1.841 and 1.096 Å, respectively.[20)] A tetrahedral P atom and a tetrahedral C atom of the methyl group were assumed. VII: The geometry of the C_4H_4P–$C_{(Me)}$ group was assumed to be identical with that of the same group in 1-benzylphosphole, whose geometry has been established by the X-ray diffraction method.[21)] The $C_{(ring)}$–H and $C_{(Me)}$–H bond lengths were assumed to be 1.084 and 1.096 Å, respectively.[20)] The C atom of the methyl group was placed on the plane of the phosphole ring,[22)] and a tetrahedral C atom of the methyl group was assumed. One of the three H atoms of the methyl group was placed perpendicularly above the phosphole ring plane. VIII: The geometry established from the microwave spectral data[23a)] was used. IX: The geometry of the $C_{(ar)}$–S–H group was taken from the data optimized by *ab initio* calculation.[24)] X: The $C_{(ar)}$–S–$C_{(Me)}$ angle was assumed to be 105°.[20)] The S–$C_{(Me)}$ and $C_{(Me)}$–H bond lengths were assumed to be 1.817 and 1.096 Å, respectively.[20)] A tetrahedral C atom of the methyl group was assumed. XI: The geometry established from the microwave spectral data[25)] was used. XII: The geometry used by Pfister–Guillouzo *et al.*[6)] for their CNDO/S calculation was adopted. XIII: The geometry established from the microwave spectral data[25)] was used. XIV: The geometry of the $C_{(ar)}$–$SOCH_3$ group was assumed to be identical with that of the same group in methyl-*p*-tolyl sulfoxide, whose geometry has been established by the X-ray diffraction method.[26)] XV: The geometry of the $C_{(ar)}$–SO_2CH_3 group was assumed to be identical with that of the same group in 1-methylsulfonyl-2-phenylsulfonylethane, whose geometry has been established by the X-ray diffraction method.[27)] XVI: The geometry of the $C_{(ar)}$–SO_2NH_2 group was assumed to be identical with that of the same group in γ-sulfanylamide, whose geometry has been established by the X-ray diffraction method.[28] The N–H bond length was assumed to be 1.013 Å.[20] XVII: The C–Cl bond length was taken from the X-ray diffraction data.[29] XVIII and XIX: All of the C–Cl bond lengths of these compounds were assumed to be identical with that of XVII. XX: The C–Cl bond length was assumed to be identical with that in XVII. The geometry of the pyridine ring was taken from the table.[20] XXI: The $C_{(ar)}$–C, C–H and C–Cl bond lengths were assumed to be 1.505, 1.101 and 1.767 Å, respectively.[20] The Cl atom was placed perpendicularly above the phenyl ring plane.[30]

Results and Discussion

The correlation of the calculated transition energies of all the compounds with the observed values will be discussed.

Although the ionization potential (IP) for the removal of an electron from each of the different orbitals in a molecule is given, rigorously speaking, by the energy difference between the ground electronic state and the ionic state of the molecule, Koopmans' theorem is well-known to be useful as a good approximation in the theoretical study of IP.[31] In the present investigation, calculated orbital energies will be compared with observed IPs by assuming the validity of Koopmans' theorem. The sequences of calculated orbital energies will also be compared with the sequences of orbitals which have been established experimentally or by quantum chemical calculations. Calculated dipole moments of all compounds are given in Table X.

In all of these discussions, previous calculation results obtained by all-valence-electron self-consistent field methods or *ab initio* methods are cited, where relevant.

Si-Containing Compounds (I—III)

Two different types of compounds (I, II) and a derivative of II were used.

I——The electronic state of I has been calculated by Reyes and Canuto[32] and by Sauer *et al.*[33] using the INDO/S method. The transition energies calculated by the former researchers coincided fairly well, but those calculated by the latter group did not coincide well, with the observed values.[34] The calculated transition energies and oscillator strengths (*f*) of I—III obtained in this work are given in Table III. The calculated transition energies of I coincide well with the observed values. The lowest excited singlet state was assigned as the $^1B_1$ $(\pi$–$\sigma^*)$ state. The next three low-lying excited singlet states were assigned as $^1B_2$ $(\pi$–$\pi^*)$, $^1A_1$ $(\pi$–$\pi^*)$ and $^1B_2$ $(\pi$–$\pi^*)$.

Solouki *et al.* have investigated the photoelectron spectrum (PES) of I, and have assigned the IPs 8.0, 9.3, *ca.* 10.7 and 11.3 eV to ionizations from $b_1(\pi)$, $a_2(\pi)$, b_2 and $b_1(\pi)$ bonding orbitals, respectively, from the results of MNDO calculation.[35] The results of the present investigation (Table III) gave the same ordering of the outermost three orbitals of the ground electronic state of I as that given by Solouki *et al.*, but the fourth orbital was assigned as $a_1(\sigma)$. The ordering of the orbitals of I given by our calculation is identical with that given by the INDO/S calculation.[32,33]

The dipole moment of I was predicted to be 0.09 D (debye).

II——Sauer *et al.*[33] have calculated the transition energies of II by the INDO/S method and obtained results which coincided fairly well with the observed values.[36] The calculated values obtained in this work (Table III) coincide very well with the observed values. All three observed transitions were assigned to π–π^* excitations.

McLean has investigated the PES of II, and has assigned the IPs at 9.18, 9.43 and 11.0 eV to ionizations from σ, π and σ bonding orbitals, respectively.[37] The energies of the occupied orbitals of II calculated by the INDO/S method[33] did not coincide well with the magnitudes of observed IPs. The results of the present investigation (Table III) indicated that the energies of the outermost three π, π and σ orbitals coincide very well with the magnitudes of the observed IPs.

Table III. Results of CNDO/S Calculations of Compounds I—III

	Electronic transition				Ionization potential			
Compound No. (Sym)	Obsd	Calcd			Obsd		Calcd	
	Energy ($\log \varepsilon$) (eV)	Energy (f) (eV)	Sym	Type	Energy (eV)	Assign	Energy (eV)	Assign
I (C_{2v})	3.88[a]	3.97 (0.12)	$^1B_1$	π–σ^*	8.0[b]	b_1 π[b]	8.86	b_1 π
	3.96				9.3	a_2 π	10.07	a_2 π
	4.06	4.08 (0.10)	$^1B_2$	π–π^*	*ca.* 10.7	b_2 σ	11.31	b_2 σ
	4.56	4.48 (0.21)	$^1A_1$	π–π^*	11.3	b_1 π	12.30	a_1 σ
		5.17 (0.0)	$^1A_2$	σ–π^*			13.82	b_1 π
		5.51 (0.01)	$^1B_1$	σ–π^*			14.00	a_1 σ
	5.85	5.51 (0.55)	$^1B_2$	π–π^*			15.38	b_2 σ
		5.65 (0.00)	$^1A_2$	π–σ^*			16.20	a_1 σ
		5.99 (0.02)	$^1B_1$	π–σ^*			17.13	a_1 σ
		6.12 (0.08)	$^1A_1$	π–π^*			21.19	a_1 σ
II (C_s)	4.71 (2.40)[c]	4.80 (0.00)	$^1A'$	π–π^*	9.18[d]	σ[d]	9.69	a'' π
		5.36 (0.01)	$^1A''$	σ–π^*	9.43	π	9.83	a'' π
		5.81 (0.0)	$^1A''$	σ–π^*	11.0	σ	10.95	a' σ
	5.77 (3.90)	5.97 (0.07)	$^1A'$	π–π^*			12.33	a' σ
	6.46 (4.76)	6.64 (1.16)	$^1A'$	π–π^*			13.83	a'' π
		6.80 (1.02)	$^1A'$	π–π^*			14.02	a' σ
III	4.81 (2.50)[c]	4.79 (0.00)		π–π^*	9.05[e]	π[e]	9.64	π
		5.20 (0.01)		σ–π^*	9.30	π	9.83	π
		5.69 (0.0)		σ–π^*	10.10	σ	10.63	σ
	5.82 (3.95)	5.92 (0.13)		π–π^*	10.70	σ	11.71	σ
	6.53 (*ca.* 4.85)	6.61 (1.18)		π–π^*	—	σ	12.27	π
		6.78 (0.96)		π–π^*	11.60	σ	12.43	σ
					12.05	π	13.82	σ
					12.8	σ	14.31	π

a) Ref. 34; in the vapor phase. *b*) Ref. 35. *c*) Ref. 36; in heptane. *d*) Ref. 37. *e*) Ref. 39.

The dipole moment of II has been measured in cyclohexane at 20 °C and found to be 0.88 ± 0.03 D.[38] The present method of calculation gave the value of 0.38 D.

III——The transition energies of III have not yet been calculated. Calculated transition energies obtained in this work (Table III) coincide very well with the observed values.[36] All three observed transitions were assigned to π–π^* excitations.

Veszprémi *et al.* have investigated the PES of III, and have assigned all the observed bands on the basis of the results of CNDO/S calculation and also the results of comparison of the Penning spectrum of III with those of tetramethylsilane, benzene and III.[39]

The calculated orbital energies obtained here (Table III) coincided much better than those calculated by Veszprémi *et al.* with the magnitudes of observed IPs. The ordering of orbitals obtained in this investigation was identical with that given by Veszprémi *et al.* except for the fifth, seventh and eighth orbitals which were assigned here as π, σ and π orbitals, respectively.

The dipole moment of III has been measured in the liquid state at 25 °C and was found to be 0.25 D.[40] The present method of calculation gave the value of 0.47 D.

From all of the results mentioned above, the parameters of the Si atom selected in this investigation are expected to be useful in calculations of the electronic states of many other Si-containing aromatic and heterocyclic compounds.

P-Containing Compounds (IV—VII)

Three diferent types of compounds (IV, V and VII) and a derivative of V were used.

IV——Schulte and Schweig[4] have calculated the electronic state of IV by the CNDO/S method, and have assigned three observed excited singlet states[41] as $^{1}B_{1}(n-\pi^{*})$, $^{1}B_{2}(\pi-\pi^{*})$ and $^{1}A_{1}(\pi-\pi^{*})$ excited states. The calculated transition energies obtained in this work (Table IV) coincide very well with the observed values. Three observed excited singlet states were assigned as $^{1}B_{1}(n-\pi^{*})$, $^{1}A_{1}(\pi-\pi^{*})$ and $^{1}B_{2}(\pi-\pi^{*})$ excited states.

Batich *et al.* have investigated the PES of IV, and have assigned the IPs at 9.2, 9.8, 10.0, 11.5 and 12.1 eV to ionizations from π, π, σ, σ and π bonding orbitals, respectively, on the basis of the results of *ab initio* calculation.[42] The results of the present investigation (Table

TABLE IV. Results of CNDO/S Calculations of Compounds IV—VII

Compound No. (Sym)	Electronic transition				Ionization potential			
	Obsd	Calcd			Obsd		Calcd	
	Energy (log ε) (eV)	Energy (f) (eV)	Sym	Type	Energy (eV)	Assign	Energy (eV)	Assign
IV (C_{2v})	4.28 (2.40)[a]	4.17 (0.07)	$^{1}B_{1}$	$n-\pi^{*}$	9.2[b]	b_1 π[b]	9.44	b_1 π
		4.36 (0.01)	$^{1}B_{2}$	$\pi-\pi^{*}$	9.8	a_2 π	9.91	a_2 π
	5.04 (3.93)	5.01 (0.25)	$^{1}A_{1}$	$\pi-\pi^{*}$	10.0	a_1 σ	11.04	a_1 n
		5.43 (0.0)	$^{1}A_{2}$	$n-\pi^{*}$	11.5	b_2 σ	11.95	b_2 σ
	5.82 (4.28)	5.88 (0.68)	$^{1}B_{2}$	$\pi-\pi^{*}$	12.1	b_1 π	13.87	b_1 π
		6.01 (0.0)	$^{1}A_{2}$	$\sigma-\pi^{*}$			14.03	a_1 σ
		6.31 (0.00)	$^{1}B_{1}$	$\sigma-\pi^{*}$			15.71	b_2 σ
		6.37 (0.71)	$^{1}A_{1}$	$\pi-\pi^{*}$			16.27	b_2 σ
V (C_s)	4.66 (2.75)[c]	4.67 (0.00)	$^{1}A''$	$\pi-\pi^{*}$	8.88[d]	π[d]	9.27	a′ π
	5.23 (3.72)	5.28 (0.44)	$^{1}A'$	$\pi-\pi^{*}$	9.37	π	9.87	a″ π
		5.98 (0.06)	$^{1}A'$	$\pi-\sigma^{*}$	10.14	n	11.19	a′ n
	5.64 (3.87)	6.03 (0.07)	$^{1}A''$	$\pi-\pi^{*}$			12.14	a′ π
		6.11 (0.01)	$^{1}A'$	$n-\pi^{*}$			12.36	a″ σ
		6.19 (0.20)	$^{1}A''$	$n-\pi^{*}$			14.53	a′ π
		6.37 (0.45)	$^{1}A'$	$\pi-\pi^{*}$			15.04	a″ σ
VI (C_s)		4.63 (0.00)	$^{1}A''$	$\pi-\pi^{*}$	8.31[e]		9.03	a′ π
	4.92 (3.70)[c]	4.92 (0.37)	$^{1}A'$	$\pi-\pi^{*}$	8.83		9.85	a″ π
	5.64 (3.88)	5.61 (0.11)	$^{1}A''$	$\pi-\pi^{*}$	9.15		10.63	a′ n
		5.67 (0.13)	$^{1}A'$	$\pi-\sigma^{*}$			11.80	a′ σ
		5.92 (0.03)	$^{1}A''$	$n-\pi^{*}$			12.21	a″ σ
		5.93 (0.14)	$^{1}A'$	$\pi-\sigma^{*}$			13.47	a″ σ
		6.00 (0.15)	$^{1}A''$	$\pi-\sigma^{*}$			14.04	a′ σ
		6.04 (0.01)	$^{1}A'$	$n-\pi^{*}$			14.55	a′ π
	5.90 (4.11)	6.24 (0.20)	$^{1}A'$	$\pi-\pi^{*}$			15.23	a″ σ
VII (C_s)		3.79 (0.18)	$^{1}A''$	$\pi-\sigma^{*}$			8.65	a″ π
	4.33 (3.89)[f]	4.34 (0.29)	$^{1}A'$	$\pi-\pi^{*}$			9.18	a″ π
		4.68 (0.00)	$^{1}A''$	$\pi-\sigma^{*}$			12.45	a′ σ
		5.10 (0.20)	$^{1}A'$	$\pi-\pi^{*}$			12.82	a′ σ
		5.31 (0.07)	$^{1}A''$	$\pi-\sigma^{*}$			13.83	a″ π
		5.39 (0.29)	$^{1}A'$	$\pi-\pi^{*}$			14.13	a′ σ
		5.50 (0.0)	$^{1}A'$	$\pi-\sigma^{*}$			14.31	a′ σ
		5.77 (0.10)	$^{1}A'$	$\pi-\pi^{*}$				
		6.41 (0.01)	$^{1}A''$	$\pi-\sigma^{*}$				
	6.2 (*ca.* 4.0)[g]	6.67 (0.02)	$^{1}A'$	$\pi-\pi^{*}$				

a) Ref. 41; in cyclohexane. *b*) Ref. 42. *c*) Ref. 44; in cyclohexane. *d*) Ref. 46. *e*) Ref. 45. *f*) Ref. 49; in isooctane. *g*) End absorption.

IV) gave the same ordering of orbitals except for the third one which was assigned here as n. Calculated orbital energies obtained in this investigation coincide fairly well with the magnitudes of observed IPs.

The dipole moment of IV has been measured in cyclohexane and was found to be 1.46 ± 0.4 D.[43] The present method of calculation gave the value of 2.28 D.

V——The calculated transition energies of V obtained in this work (Table IV) coincide very well with observed values.[44] All three observed transitions were assigned to π–π^* excitations.

IPs of V have been measured by two groups of researchers,[45,46] and those measured by Cabelli *et al.*[46] were adopted in this investigation as the observed values. Three observed IPs have been attributed to ionizations from either n, π and π bonding orbitals on the basis of the results of CNDO/2 calculation,[45] or π, π and n bonding orbitals on the basis of the results of MNDO calculation.[46] The latter ordering of orbitals has also been obtained by CNDO/2 calculation performed by Schmidt *et al.*[47] The present method of calculation supported the latter ordering of orbitals (Table IV).

The dipole moment of V has been measured in hexane at 20 °C and found to be 1.11 D.[48] The present method of calculation gave the value of 2.51 D.

VI——The calculated transition energies of VI obtained in this work are given in Table IV, and they coincide very well with the observed values.[44] All three observed transitions were assigned to π–π^* excitations.

According to the results of CNDO/S calculation of VI performed by Schmidt *et al.*,[47] three observed IPs at 8.31, 8.83 and 9.15 eV[45] can be attributed to the ionizations from π, n and π bonding orbitals, respectively. The results of the present investigation (Table IV) indicated that these three bonding orbitals are in the order π, π and n.

The dipole moment of VI was found to be 1.31 D in hexane at 20 °C.[48] The present method of calculation gave the value of 2.98 D.

VII——The calculated transition energies of VII obtained in this work are given in Table IV. The calculated lowest excited singlet state (π–σ^*) having the theoretical oscillator strength of 0.18 has no experimental counterpart.[49] Both the observed absorption maximum at 285.7 nm and the strong end absorption were attributed to π–π^* excitations. The coincidence of the calculated transition energies with observed values was excellent. Calculated orbital energies are given in Table IV. The dipole moment of VII was predicted to be 2.72 D.

From all of the results mentioned above, the parameters of the P atom selected in this investigation are expected to be useful in calculations of the electronic states of many other P-containing aromatic and heterocyclic compounds.

S-Containing Compounds(VIII—XVI)

Seven different types of compounds (VIII, IX, XI, XII, XIV—XVI), a derivative of IX and a compound (XIII) containing two S atoms, whose chemical environments are different from each other, were used.

VIII——The ultraviolet absorption maximum of VIII has been reported to be observed at 231 nm (43300 cm^{-1}) in hexane[50] and in isooctane.[51] In the vapor phase, Lonardo *et al.* have observed three 0–0 bands at 41595, 48330 and 53270 cm^{-1}.[52] In this investigation, observed values measured in the vapor phase were used (Table V).

Transition energies of VIII have been calculated by a procedure similar to the INDO method,[53] by the CNDO/S method,[4] by the INDO/S method,[54] by the CINDO/SHIFT/UV method,[54] by the VCNDO/S method[9] and by the *ab initio* method.[55] Among the results of these investigations, only two (obtained by the CNDO/S and the INDO/S methods) coincided fairly well with observed values. The calculated transition energies obtained in this work (Table V) coincide very well with the observed values. The three observed excited singlet states were assigned as $^1B_2(\pi\text{–}\pi^*)$, $^1B_2(\pi\text{–}\pi^*)$ and $^1A_1(\pi\text{–}\pi^*)$.

Klasinc *et al.* have investigated the PES of VIII and assigned IPs to ionizations from $a_2\pi$, $b_1\pi$, a_1n, $b_1\pi$, b_2, a_1 and b_2 orbitals, respectively, on the basis of both the observed He^{II}/He^{I} intensity changes and the results of INDO/RZ calculation.[56] Buemi *et al.*[57] have also performed calculations of the orbital energies of VIII by the *ab initio* method using the minimal STO-3G basis sets, by the INDO/S method and by the CNDO/S method; the orderings of orbitals were as follows:

$a_2\pi < b_1\pi < a_1n < b_1\pi \sim a_1 \sim b_2 < b_2$ (*ab initio*)

$a_2\pi < b_1\pi < a_1n < a_1 < b_2 < b_1\pi < b_2$ (INDO/S)

$a_2\pi < b_1\pi < a_1n < a_1 \sim b_2 < b_2 < b_1\pi$(CNDO/S)

The present method of calculation gave the same ordering of orbitals as that given by the INDO/S method (Table V). With regard to the coincidence of calculated orbital energies with

TABLE V. Results of CNDO/S Calculations of Compounds VIII—X

	Electronic transition				Ionization potential			
Compound No. (Sym)	Obsd	Calcd			Obsd		Calcd	
	Energy (log ε) (eV)	Energy (*f*) (eV)	Sym	Type	Energy (eV)	Assign	Energy (eV)	Assign
VIII (C_{2v})		4.85 (0.20)	$^1A_1$	π–π^*	8.85[b]	a_2 π[b]	9.36	a_2 π
	5.16[a]	5.28 (0.14)	$^1B_2$	π–π^*	9.49	b_1 π	9.50	b_1 π
		5.70 (0.00)	$^1A_2$	π–σ^*	12.00	a_1 n	11.99	a_1 n
		6.06 (0.25)	$^1B_1$	π–σ^*	12.46	b_1 π	13.73	a_1 σ
	5.99 (weak)	6.15 (0.26)	$^1B_2$	π–π^*	13.11	b_2 σ	13.82	b_2 σ
		6.25 (0.05)	$^1B_1$	n–π^*	13.80	a_1 σ	14.16	b_1 π
		6.33 (0.00)	$^1B_1$	π–σ^*	14.23	b_2 σ	14.23	b_2 σ
		6.48 (0.01)	$^1B_1$	π–σ^*			19.62	a_1 σ
	6.60 (strong)	6.63 (0.54)	$^1A_1$	π–π^*			21.96	b_2 σ
IX	4.49 (2.85)[c]	4.55 (0.01)		π–π^*	8.49[d]		8.91	π
	5.28 (3.93)	5.02 (0.51)		π–π^*	9.41		9.98	π
		5.35 (0.00)		π–σ^*	10.61		11.19	π
		5.73 (0.26)		π–σ^*	11.61		11.71	n
		5.97 (0.08)		π–π^*	12.22		12.43	σ
		6.06 (0.00)		π–σ^*	13.14		13.40	σ
		6.18 (0.19)		π–π^*	14.17		14.72	π
	6.11 (4.34)	6.29 (0.68)		π–π^*	14.42		14.93	σ
		6.42 (0.00)		n–π^*	15.12		15.78	σ
		6.57 (0.00)		n–π^*	15.64		17.00	σ
	ca. 6.70 (4.20)	6.58 (0.31)		π–π^*	16.71		17.74	σ
X	4.43 (3.18)[c]	4.51 (0.01)		π–π^*	8.07[e]	π[e]	8.70	π
	4.88 (3.99)	4.83 (0.50)		π–π^*	9.28	π	9.93	π
		5.30 (0.00)		π–σ^*	10.14	π	10.87	π
		5.48 (0.23)		π–σ^*	11.1	n	11.39	n
	5.82 (3.90)	5.80 (0.12)		π–π^*	11.9	σ	12.24	σ
		5.86 (0.01)		π–σ^*			12.95	σ
		6.04 (0.09)		π–π^*			14.33	σ
	6.11 (4.15)	6.13 (0.48)		π–π^*			14.54	π
		6.28 (0.00)		n–π^*			15.56	σ
	6.74 (4.41)	6.49 (0.30)		π–π^*			16.67	σ

a) Ref. 52; in the vapor phase. *b*) Ref. 56. *c*) Ref. 36; in heptane. *d*) Ref. 31. *e*) Ref. 58.

the magnitudes of observed IPs, there were no significant differences between the results of the four semi-empirical calculations, including the present method of calculation.

The dipole moment of VIII has been measured the vapor phase to be about 0.6 D.[23a,23b] The present method of calculation gave the value of 1.23 D.

IX, X——The VCNDO/S method has been used to calculate the transition energies of IX,[9] but the results have not been satisfactory. The transition energies of two compounds calculated in this work are given in Table V. In both compounds, the coincidence of calculated transition energies with observed values[36] was very satisfactory. All four observed transitions of IX and all five observed transitions of X were assigned to π–π^* excitations.

From the results of the present investigation (Table V), eleven bands observed in the PES of IX[31] and five bands observed in the PES of X[58] were assigned to ionizations from π, π, π, n, σ, σ, π, σ, σ, σ and σ orbitals, and π, π, π, n and σ orbitals, respectively. The coincidence of the calculated orbital energies with the magnitudes of observed IPs were very satisfactory in both compounds.

The dipole moments of IX and X have been measured in benzene at 25 °C as 1.23 D[59] and in benzene at 30 °C as 1.31 D,[60] respectively. The present method of calculation gave the values of 2.01 and 2.38 D, respectively.

XI—XIII——Transition energies of XI, XII and XIII have been calculated by the CNDO/S method[6] and by the VCNDO/S method,[9] and fairly satisfactory results have been

TABLE VI. Results of CNDO/S Calculations of Compounds XI—XIII

Compound No. (Sym)	Electronic transition				Ionization potential			
	Obsd	Calcd			Obsd		Calcd	
	Energy (log ε) (eV)	Energy (f) (eV)	Sym	Type	Energy (eV)	Assign	Energy (eV)	Assign
XI (C_{2v})	2.25 (1.26)[a]	1.66 (0.0)	$^1A_2$	n–π^*	8.10[b]	b_2 n[b]	8.63	b_2 n_S
	3.76 (4.22)	3.64 (0.84)	$^1A_1$	π–π^*	8.44	b_1 π	8.80	b_1 π
		4.55 (0.00)	$^1B_1$	n–π^*	10.66	a_2 π	11.07	a_2 π
		4.55 (0.00)	$^1B_2$	π–π^*	11.60		12.40	a_1 σ
		5.02 (0.02)	$^1B_1$	σ–π^*			13.33	b_1 π
	5.39 (3.78)	5.07 (0.11)	$^1B_2$	π–π^*			13.92	b_2 σ
							15.18	a_1 σ
XII (C_{2v})	3.9 (1.72)[a]	3.04 (0.0)	$^1A_2$	n–π^*	8.97[b]	b_1 π[b]	9.33	b_1 π
	4.43 (4.19)	4.35 (0.72)	$^1A_1$	π–π^*	9.25	b_2 n	11.00	b_2 n_O
		4.77 (0.10)	$^1B_2$	π–π^*	10.73	a_2 π	11.06	a_2 π
	5.64 (3.67)	5.61 (0.15)	$^1B_2$	π–π^*	11.91		12.29	b_1 π
							12.53	a_1 σ
							13.24	b_2 σ
							14.25	a_1 σ
XIII (C_{2v})	2.1 (1.43)[a]	1.67 (0.0)	$^1A_2$	n–π^*	7.96[b]	b_2 n[b]	8.27	b_1 π
	3.26 (4.32)	3.26 (1.06)	$^1A_1$	π–π^*	8.11	b_1 π	8.42	b_2 n
	4.28 (sh)	4.05 (0.02)	$^1B_2$	π–π^*	10.50	a_2 π	11.15	a_2 π
		4.39 (0.00)	$^1B_1$	n–π^*	11.9		11.31	b_1 π
		5.03 (0.02)	$^1B_1$	σ–π^*			11.88	a_1 σ
	5.14 (3.34)	5.27 (0.10)	$^1B_2$	π–π^*			12.53	b_2 σ
							13.08	a_1 σ
							14.81	b_1 π
							16.51	b_2 σ

a) Ref. 6; in cyclohexane. *b*) Ref. 61.

obtained in all three compounds. The calculated transition energies obtained in this work also coincide satisfactorily with observed values[6] in all cases (Table VI).

Colonna *et al.*[61] investigated the PES of XI, XII and XIII, and ordered the outermost orbitals of the three compounds on the bases of experimental evidence as follows: XI, $b_2n < b_1\pi < a_2\pi$; XII, $b_1\pi < b_2n < a_2\pi$; XIII, $b_2n < b_1\pi < a_2\pi$. They also performed calculations of the orbital energies of the three compounds by the CNDO/2 method,[61] and obtained the following sequences of the outermost orbitals: XI, $b_1\pi \sim b_2n < a_1 < b_2 < a_2\pi < a_1 \sim b_1\pi$; XII, $b_1\pi < b_2n < a_1 < b_2 < a_2\pi \sim b_1\pi < a_1$; XIII, $b_1\pi < b_2n < a_1 < b_2 < b_1\pi < a_1 < a_2\pi < a_1 \sim b_2$. The present method of calculation gave the orderings of the outermost orbitals shown in Table VI. The calculated orbital energies obtained in this work coincide satisfactorily with the magnitudes of observed IPs in all three compounds.

The dipole moments of the three compounds have been measured to be 4.08 ± 0.01, 3.96 ± 0.02 and 4.41 ± 0.03 D, respectively.[62] The present method of calculation gave the values of 4.45, 6.18 and 5.72 D, respectively.

XIV, XV——Singerman and Jaffé[9] have calculated the transition energies of XIV and XV by the VCNDO/S method and compared the calculated values with observed values, but they did not give the source of the absorption data. In this investigation, therefore, the spectral data for XIV reported by Leandri *et al.*[63] and those for XV reported by Shorygin *et al.*[36] were used as the observed transition energies. The calculated transition energies of the two compounds obtained in this work and the assignments of excited singlet states are given in Table VII. The coincidence of the calculated values with observed transition energies were satisfactory in both cases.

TABLE VII. Results of CNDO/S Calculations of Compounds XIV—XVI

Compound No.	Electronic transition			Ionization potential		
	Obsd	Calcd		Obsd	Calcd	
	Energy (log ε) (eV)	Energy (f) (eV)	Type	Energy (eV)	Energy (eV)	Assign
XIV	4.90 (3.60)[a]	4.73 (0.00)	π–π*	8.85[b]	9.50	π
		5.27 (0.13)	π–π*	9.7	10.01	π
		5.77 (0.17)	π–π*	9.7	10.20	π
		5.97 (0.04)	π–σ*	10.00	10.69	n_O
		6.00 (0.07)	π–σ*		12.20	σ
		6.05 (0.02)	π–π*		12.37	σ
		6.28 (0.09)	n–π*		12.80	σ
XV	4.70 (3.00)[c]	4.77 (0.00)	π–π*	9.85[b]	10.09	π
		5.62 (0.01)	π–π*	9.85	10.14	π
	5.77 (3.90)	5.88 (0.13)	π–π*	10.58	10.61	π
		6.29 (0.00)	π–π*	11.05	11.38	n_O
	6.56 (4.76)	6.59 (0.59)	π–π*	11.9	11.58	π
		6.71 (0.24)	n–π*		12.10	n_O
		6.74 (0.66)	π–π*		12.66	σ
XVI	4.59 (strong)[d]	4.78 (0.01)	π–π*		10.17	π
		5.68 (0.06)	π–π*		10.19	π
		5.99 (0.05)	π–π*		10.94	π
		6.39 (0.05)	π–π*		11.40	n_O
		6.60 (0.02)	n–π*		11.78	n_O
		6.71 (0.92)	π–π*		12.00	π

a) Ref. 63; in cyclohexane. *b*) Ref. 64. *c*) Ref. 36; in heptane. *d*) Ref. 67; in the vapor phase.

PES of XIV and XV have been investigated by Mohraz *et al.*[64] Orbital energies of the two compounds, however, have not yet been calculated by any quantum chemical method.

The calculated orbital energies of XIV and XV obtained in this work coincide very satisfactorily with the magnitudes of observed IPs. The calculations also give the ordering of the outermost four orbitals of XIV and that of the outermost five orbitals of XV as shown in Table VII.

The dipole moments of XIV and XV have been measured in benzene at 25 °C as 3.88 D[65] and in benzene at 30 °C as 4.80 D,[66] respectively. The present method of calculation gave the values of 5.78 and 7.12 D, respectively.

XVI——The calculated transition energies of XVI obtained in this work are given in Table VII. The calculated value of the lowest excited singlet state coincides well with the observed value measured in the vapor phase.[67]

The IP of XVI has not yet been measured. Calculated energies of the outermost several orbitals are given in Table VII.

The dipole moment of XVI has been measured in dioxane and benzene at 25 °C and found to be 5.09 and 4.73 D, respectively.[68] The present method of calculation gave the value of 7.25 D.

From all of the results mentioned above, the parameters of the S atom selected in this investigation are expected to be useful in calculations of the electronic states of many other S-containing aromatic and heterocyclic compounds.

Cl-Containing Compounds (XVII—XXI)

Four compounds (XVII—XX) in which the Cl atom(s) is directly conjugated to an aromatic or a heterocyclic ring, and a compound (XXI) in which the Cl atom is indirectly conjugated to an aromatic ring, were used.

XVII—XIX——Transition energies of XVII, XVIII and XIX have been calculated by the CNDO/S method, and the calculated values have been compared with observed values measured in the vapor phase.[10] The transition energies of the three compounds calculated in this work are given in Table VIII. The coincidence of calculated transition energies with observed values for XVII,[36] for XVIII,[69,70] and for XIX[69,70] were very satisfactory.

PES of XVII and XVIII have been measured by Potts *et al.*[71] and by Ruščić *et al.*,[72] and PES of XIX has also been measured by the latter group (Table VIII). Observed PES bands of XVII and XVIII have been correlated with particular orbitals of the respective compounds by both groups of researchers. The ordering of the outermost ten orbitals of XVII has been assigned by Ruščić *et al.* on the basis of the shapes and intensities of PES band systems and vibrational fine structure as follows:

$$b_1 < a_2 < b_2 < b_1 < a_1 < b_2 < b_1 < a_1 < b_2 < b_2 \text{ (Table VIII)}$$

The results of *ab initio* calculation (using the minimal basis sets of contradicted Gaussian orbitals) performed by Ruščić *et al.* and those of *ab initio* calculation (using the minimal STO-3G basis sets) performed by Potts *et al.* supported this ordering. The present method of calculation gave the same ordering of orbitals as above (Table VIII).

The ordering of the outermost ten orbitals of XVIII has been assigned by Ruščić *et al.* on the basis of experiments as follows:

$$b_{2g} < b_{1g} < b_{3u} \sim b_{2u} \sim b_{3g} < b_{2g} \sim a_g < b_{3u} < b_{3g} < b_{1u} \text{ (Table VIII)}$$

A slightly different ordering of the same orbitals has also been made, based on *ab initio* calculations. Namely, Ruščić *et al.* have predicted the ordering of $b_{2g} < b_{1g} < b_{2u} \sim b_{3u} \sim b_{3g} < b_{2g} \sim a_g < b_{3g} < b_{1u} < b_{3u}$, and Potts *et al.* have presented the ordering of $b_{2g} < b_{1g} < b_{2u} \sim b_{3g} \sim b_{3u} < a_g \sim b_{2g} < b_{3g} < b_{1u} < b_{3u}$. The ordering of orbitals given by the present method of calculation was identical with that given by Potts *et al.*

Ruščić *et al.* have assigned two kinds of orderings of the outermost ten orbitals of XIX, one based on experiments and the other based on the results of *ab initio* calculation, as follows:

$a_2 < b_1 < b_1 \sim b_2 \sim a_1 < a_2 \sim b_2 < b_1 < a_1 < a_1$ (experiments, Table VIII)

$a_2 < b_1 < b_2 < a_1 < b_1 < a_2 < b_2 < a_1 < b_1 < a_1$ (calculation)

The present method of calculation gave the ordering of $a_2 < b_1 < b_2 \sim a_1 < b_1 < b_2 < a_2 \sim a_1 < b_2 \sim b_1$ (Table VIII).

The dipole moments of XVII and XIX have been measured in the vapor phase as 1.69 ± 0.01 D[73] and 1.67 D,[74] respectively. The present method of calculation gave the values of 2.48 and 2.42 D, respectively.

TABLE VIII. Results of CNDO/S Calculations of Compounds XVII—XIX

Compound No. (Sym)	Electronic transition				Ionization potential			
	Obsd	Calcd			Obsd		Calcd	
	Energy (log ε) (eV)	Energy (*f*) (eV)	Sym	Type	Energy (eV)	Assign	Energy (eV)	Assign
XVII (C_{2v})	4.75 (2.43)[a]	4.71 (0.00)	$^1B_2$	π–π^*	9.07[b]	b_1 π[b]	9.75	b_1 π
	5.79 (3.90)	5.71 (0.22)	$^1A_1$	π–π^*	9.64	a_2 π	10.16	a_2 π
		6.29 (0.0)	$^1A_2$	n–π^*	11.31	b_2 n	11.28	b_2 n
	6.56 (4.79)	6.55 (0.93)	$^1B_2$	π–π^*	11.67	b_1 π	12.25	b_1 π
		6.58 (0.95)	$^1A_1$	π–π^*	12.26	a_1 σ	12.54	a_1 σ
					12.98	b_2 σ	12.83	b_2 σ
					13.21	b_1 π	15.00	b_1 π
					14.41	a_1 σ	15.29	a_1 σ
					14.85	b_2 σ	15.94	b_2 σ
					15.53	b_2 σ	17.13	b_2 σ
XVIII (D_{2h})	4.54 (2.70)[c]	4.59 (0.00)	$^1B_{2u}$	π–π^*	8.97[b]	b_{2g} π[b]	9.68	b_{2g} π
	5.51 (4.13)[c]	5.40 (0.40)	$^1B_{1u}$	π–π^*	9.84	b_{1g} π	10.40	b_{1g} π
		6.14 (0.00)	$^1B_{2g}$	σ–π^*	11.37	b_{3u} π	11.39	b_{2u} n
	6.42[d]	6.35 (0.94)	$^1B_{2u}$	π–π^*	11.50	b_{2u} n	11.48	b_{3g} n
		6.48 (0.00)	$^1B_{1g}$	n–π^*	—	b_{3g} n	11.74	b_{3u} π
		6.57 (0.95)	$^1B_{1u}$	π–π^*	12.78	b_{2g} π	12.65	a_g σ
					12.91	a_g σ	13.06	b_{2g} π
					—	b_{3u} π	13.24	b_{3g} σ
					13.44	b_{3g} σ	14.94	b_{1u} σ
					14.54	b_{1u} σ	15.46	b_{3u} π
XIX (C_{2v})	4.59 (2.57)[c]	4.58 (0.00)	$^1B_2$	π–π^*	9.14[b]	a_2 π[b]	9.82	a_2 π
	5.71 (3.93)[c]	5.55 (0.12)	$^1A_1$	π–π^*	9.70	b_1 π	10.14	b_1 π
	6.32[d]	6.17 (1.20)	$^1B_2$	π–π^*	11.47	b_1 π	11.34	b_2 n
		6.29 (0.0)	$^1A_2$	n–π^*	11.58	b_2 n	11.53	a_1 n
		6.36 (0.80)	$^1A_1$	π–π^*	11.73	a_1 n	11.97	b_1 π
					12.80	a_2 π	12.77	b_2 σ
					12.92	b_2 σ	12.93	a_2 π
					—	b_1 π	13.09	a_1 σ
					13.57	a_1 σ	15.40	b_2 σ
					14.62	a_1 σ	15.48	b_1 π

a) Ref. 36; in heptane. *b)* Ref. 72. *c)* Ref. 69; in cyclohexane. *d)* Ref. 70; in a non-polar solvent.

Table IX. Results of CNDO/S Calculations of Compounds XX and XXI

Compound No. (Sym)	Electronic transition				Ionization potential		
	Obsd	Calcd			Obsd	Calcd	
	Energy (log ε) (eV)	Energy (f) (eV)	Sym	Type	Energy (eV)	Energy (eV)	Assign
XX		4.39 (0.00)		n–π*	9.65[b]	9.89	π
	4.61 (3.45)[a]	4.75 (0.07)		π–π*	9.90	10.89	π
		5.62 (0.0)		n–π*	10.68	11.23	n_{Cl}
	5.82 (3.93)	5.77 (0.24)		π–π*	11.82	11.91	n_N
		6.47 (0.00)		n–π*	12.45	12.59	π
		6.53 (0.05)		π–σ*		13.17	σ
		6.67 (0.71)		π–π*		15.24	σ
XXI (C_s)	4.77 (2.40)[c]	4.72 (0.00)	$^1A''$	π–π*	9.30[d]	9.62	a′ π
	5.77 (3.90)	5.86 (0.09)	$^1A'$	π–π*	9.60	10.02	a″ π
		6.55 (0.27)	$^1A'$	σ–π*	10.90	11.25	a′ n
		6.64 (0.29)	$^1A''$	σ–π*	10.90	11.38	a″ n
	6.53 (4.68)	6.77 (0.63)	$^1A'$	π–π*		12.48	a″ σ
		6.79 (0.68)	$^1A''$	π–π*		12.61	a′ σ

a) Ref. 75; in hexane. *b*) Ref. 76. *c*) Ref. 36; in heptane. *d*) Ref. 77.

Table X. Dipole Moments

Compound	Obsd (Solvent)	Calcd	Compound	Obsd (Solvent)	Calcd
I	—	0.09	XII	3.96[h]	6.18
II	0.88 (Cyclohexane)[a]	0.38	XIII	4.41[h]	5.72
III	0.25 (Liquid)[b]	0.47	XIV	3.88 (Benzene)[i]	5.78
IV	1.46 (Cyclohexane)[c]	2.28	XV	4.80 (Benzene)[j]	7.12
V	1.11 (Hexane)[d]	2.51	XVI	5.09 (Dioxane)[k]	7.25
VI	1.31 (Hexane)[d]	2.98		4.73 (Benzene)[k]	
VII	—	2.72	XVII	1.69 (Vapor phase)[l]	2.48
VIII	0.6 (Vapor phase)[e]	1.23	XVIII	0.0 (Vapor phase)[m]	0.0
IX	1.23 (Benzene)[f]	2.01	XIX	1.67 (Vapor phase)[m]	2.42
X	1.31 (Benzene)[g]	2.38	XX	2.02 (Benzene)[n]	2.82
XI	4.08[h]	4.45	XXI	1.82 (Benzene)[o]	2.30

a) Ref. 38. *b*) Ref. 40. *c*) Ref. 43. *d*) Ref. 48. *e*) Ref. 23. *f*) Ref. 59. *g*) Ref. 60. *h*) Ref. 62. *i*) Ref. 65. *j*) Ref. 66. *k*) Ref. 68. *l*) Ref. 73. *m*) Ref. 74. *n*) Ref. 78. *o*) Ref. 79.

XX, XXI——The transition energies of XX and XXI have been calculated by the CNDO/S method, and compared with observed values (XX in the vapor phase; the state of measurement of XXI is unknown).[10] The calculated transition energies of XX and XXI obtained in this work coincide very well with the values observed in hexane[75] and in heptane,[36] respectively (Table IX).

PES of XX and XXI have been investigated by Modelli and Distefano[76] and Schmidt and Schweig,[77] respectively (Table IX). The present method of calculation gave the orderings of the outermost several orbitals of XX and XXI shown in Table IX.

The dipole moments of XX and XXI have been measured in benzene at 25 °C as 2.02 D[78] and in benzene at 25 °C as 1.82 D,[79] respectively. The present method of calculation gave the values of 2.82 and 2.30 D, respectively.

From all of the results mentioned above, the parameters of the Cl atom selected in this investigation are expected to be useful in calculations of the electronic states of many other Cl-containing aromatic and heterocyclic compounds.

Conclusion

The CNDO/S method developed by Jaffé *et al.*[1,2] was extended very successfully to the calculation of the electronic states of a variety of aromatic and heterocyclic compounds containing a second-row element (Si, P, S and Cl). The *spd* basis sets were found to be superior to the *sp* basis sets in the calculation, and the parameters of Si, P, S and Cl atoms contained in aromatic or heterocyclic compounds were optimized to reproduce observed transition energies as satisfactorily as possible. Calculated orbital energies of compounds obtained by the present method of calculation were found to coincide very well with observed values without exception.

It is expected that CNDO/S calculations using the *spd* basis sets and parameters of Si, P, S and Cl atoms selected in this work should be widely applicable to the calculation of the electronic states of many aromatic and heterocyclic compounds containing second-row elements.

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