

# The Calculation of Excited State and Ground State Properties of Conjugated Heteroatomic Molecules Using a Single SCF-LCAO-CI Method Including $\sigma$ -Polarization

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An SCF- $\pi$  method including variable  $\pi$ -electronegativity and  $\sigma$ -polarization is described and applied to the calculation of electronic transitions and ionization potentials of a large variety of heteroatomic molecules containing boron, nitrogen, oxygen, fluorine, chlorine, and sulfur. The necessary atomic parameters are the Slater effective nuclear charges and published ionization potentials, electron affinities and  $\sigma$ -orbital electronegativities for trigonally hybridized atoms. The program automatically adjusts the initial atomic parameters to reflect the molecular environment without the intervention of the user. The agreement between calculated and observed transition energies, oscillator strengths and ionization potentials is very good.

Es wird eine SCF- $\pi$ -Methode einschließlich veränderlicher  $\pi$ -Elektronegativität und  $\sigma$ -Polarisation beschrieben und auf die Berechnung von Elektronenübergängen und Ionisierungspotentialen einer großen Mannigfaltigkeit von heteroatomaren Molekülen, die Bor, Stickstoff, Sauerstoff, Fluor, Chlor und Schwefel enthalten, angewandt. Die notwendigen atomaren Parameter sind die effektiven Kernladungen nach Slater und veröffentlichte Ionisierungspotentiale, Elektronenaffinitäten und  $\sigma$ -orbitale Elektronegativitäten für trigonal hybridisierte Atome. Die ersten atomaren Parameter werden entsprechend angepaßt, um die molekulare Umgebung zu berücksichtigen. Die Übereinstimmung zwischen errechneten und beobachteten Übergangsenergien, Oszillatorenstärken und Ionisierungspotentialen ist sehr gut.

Description d'une méthode SCF- $\pi$  comportant une électronégativité  $\pi$  variable et une polarisation  $\sigma$ , et de son application au calcul des transitions électroniques et des potentiels d'ionisation d'une grande série de molécules hétéroatomiques contenant du bore, de l'azote, de l'oxygène, du fluor, du chlore et du soufre. Les paramètres atomiques requis sont les charges nucléaires effectives de Slater et les potentiels d'ionisation publiés, ainsi que les affinités électroniques et les électronégativités des orbitales  $\sigma$  pour les atomes à hybridation trigonale. Les paramètres atomiques initiaux sont ajustés de manière à refléter l'environnement moléculaire. L'accord entre les transitions, les forces oscillatrices et les potentiels d'ionisations calculés et observés est très bon.

## Introduction

In recent years many self-consistent-field molecular orbital calculations on conjugated heterocyclic molecules have appeared. According to the Pople approximations [1] for the SCF-MO treatment of planar  $\pi$ -molecules, the elements of

the Fock matrix are<sup>1</sup>

$$F_{pp} = H_{pp} + N_p \gamma_{pp} - \frac{1}{2} P_{pp} \gamma_{pp} + \sum_q (P_{qq} - N_q) \gamma_{pq}, \quad (1)$$

$$F_{pq} = H_{pq} - \frac{1}{2} P_{pq} \gamma_{pq}, \quad (2)$$

where  $H_{pp}$  [2, 3] and  $H_{pq}$  [4] may be approximated by

$$H_{pp} = -I_p \text{ (if } p \text{ contributes one electron),} \quad (3)$$

$$H_{pp} = -I_p - \gamma_{pp} \text{ (if } p \text{ contributes two electrons),} \quad (4)$$

$$H_{pq} = \text{const} \times \frac{(H_{pp} + H_{qq})}{(1 + S_{pq})} S_{pq}. \quad (5)$$

This SCF method with configuration interaction (CI) is capable of predicting fairly well the absorbance spectra of aromatic hydrocarbons and heteroaromatics if the heteroatom is bound by a not too polar bond. However, this method does not work well with molecules which have highly polar  $\sigma$ -bonds [5]. Therefore, most of the effort has been directed at obtaining a set of semi-empirical bond and atom parameters,  $H_{pq}$  and  $H_{pp}$ , that would correlate a particular property of a particular set of molecules where the effect of the polar  $\sigma$ -bonds has been included in the empirical values in some average way. However, this has necessitated a different set of empirical values for each property and for each atomic environment in which an atom might be found, and practically every study has produced a different set of parameters. Consequently, the empirical method has been limited in its predictive capability when applied to a new molecule, particularly if the molecule has highly polar bonds. The purpose of this work is to develop a method for calculating ground state and excited state properties of molecules from a knowledge of the approximate bond lengths in the molecule and from atomic properties, i.e., ionization potentials, electron affinities, Slater nuclear charges and electronegativities, determined from other data, without the use of any empirical adjustment. Some of the elements of this method have been used individually [3–14] but have not previously been brought together and applied to a wide variety of molecules.

The effect of polar  $\sigma$ -bonds on the  $\pi$ -orbitals has been discussed in textbooks by Streitwieser [15] and Dewar [16]. Pujol [5] included  $\sigma$ -polarization in an SCF treatment of furan using a perturbation method. Armstrong and Perkins examined molecules containing boron-halogen and boron-oxygen bonds and treated the  $\sigma$ -polarization directly [3]. Following Wilmhurst [6], they approximated the number of electrons,  $n_p$ , at atom  $p$  due to a diatomic  $\sigma$ -bond between  $p$  and  $q$  as

$$n_p = \frac{2\chi_p}{\chi_p + \chi_q}, \quad (6)$$

where  $\chi_p$  and  $\chi_q$  are the atomic electronegativities of the bonding orbitals. The effective nuclear charge,  $Z_p$ , of the neutral atom  $p$  was then adjusted to reflect this

<sup>1</sup>  $N_p$  is the nuclear charge of  $p$  minus its  $\pi$ -electron(s);  $P_{pq}$  is the  $pq$  element of the charge density, bond-order matrix;  $I_p$  is the ionization potential of  $p$  in its valence state;  $\gamma_{pq}$  is the repulsion integral; and  $S_{pq}$  is the overlap integral for  $p$  and  $q$ .

$\sigma$ -polarization and the new  $Z_p$  was used to recalculate  $I_p$  by means of a quadratic equation. They applied this  $\sigma$ -drift correction to calculations of the spectra of dichlorovinylborane and of divinylchloroborane to obtain a good fit of the respective UV spectra, but did not use it to fit the spectrum of trivinylborane. The  $\sigma$ -drift treatment was also sufficient to fit the spectrum of borafuorenium ion, but in order to fit the diphenylborenium ion spectrum, an arbitrary amount of the positive charge had to be removed from the boron, presumably because of solvation.

Clark and Emsley [14] also employed the Wilmhurst approximation of  $\sigma$ -polarization (Eq. (6)) in a manner similar to Armstrong *et al.*, and combined it with Murrell *et al.*'s  $\sigma$ -inductive parameters [17] in a study of four substituted benzenes. The method required the user to guess at the exact hybridizations of the atoms and to interpolate the atomic parameters. It also used different bond integrals for ground state and excited state properties.

More recently, Dewar and Morita [7] took  $\sigma$ -polarization into account by approximating the formal charges ( $\pm \delta Q$ ) on atoms X and Y, due to polarity of the  $\sigma$ -bond linking them, as an empirical constant times the difference in their  $\sigma$ -orbital electronegativities. After making corresponding adjustments to the atomic ionization potentials, they obtained good agreement between calculated and experimental ground state properties for a large number of nitrogen- and oxygen-containing molecules. They did not apply their method to excitation energies. Momicchioli [8] used  $\sigma$ -polarization corrections to  $H_{pp}$  with empirical  $H_{pq}$  for calculations on five-membered heterocycles and Nishimoto *et al.*, [9] used empirical parameters to reflect  $\sigma$ -polarization in protonated N-heterocycles.

We report here an SCF-MO-CI method which incorporates  $\sigma$ -polarization in a manner similar to that of Armstrong and Perkins [3] and Clark and Emsley [14] and apply it to a much broader spectrum of molecules than in the previous reports. The method also incorporates variable  $\pi$ -electronegativity adjustments similar to those of Brown and Heffernan [10]. We believe the method to be of great predictive value because it requires no structure-specific empirical parameters.

### Method of Calculation

The calculations were performed on an IBM 360/65 computer using an SCF-MO-CI program derived from the QCPE program No. 71 written by J. E. Bloor *et al.* [2]. Modifications were made in the QCPE program such that the Fock matrix was defined by Eqs. (1), (2), (5), and (7)–(10). The constant in Eq. (5) was set equal to 0.56 by consideration of the UV spectrum of benzene. That value gives a value of  $-2.45$  eV for the exchange integral in benzene.

$$\gamma_{pq} = \frac{14.397}{a_{pq} + r_{pq}}, \quad (7)$$

$$a_{pq} = \frac{28.794}{\gamma_{pp} + \gamma_{qq}}, \quad (8)$$

$$\gamma_{pp} = I_p - A_p, \quad (9)$$

$$H_{pp} = -I_p - (N_p - 1)\gamma_{pp}. \quad (10)$$

Table 1. Atomic parameter

$p$	$N_p$	$Z_p$	$I_p, \text{eV}^a$	$\gamma_{pp}, \text{eV}^a$	$\chi_p^a$
B	0, 1	2.25, 2.60	8.33	6.91	1.96
C	1	3.25	11.16	11.13	2.75
N	1, 2	3.90, 4.25	14.12	12.34	4.13
O	1, 2	4.55, 4.90	17.7	15.23	5.54
F	2	5.55	20.86	17.36	3.90
S	2	5.80	12.7	9.94	3.46
Cl	2	6.45	15.03	11.30	2.95

<sup>a</sup> Ref. [14].

Eqs. (7) and (8) define the Mataga approximation [11]; Eq. (9) is due to Pariser [12]. An overlap routine based on Mulliken's equations [13] was used to calculate the quantities  $S_{pq}$  required in Eq. (5). Non-nearest-neighbour bond integrals were included [18]. The formal nuclear charge,  $N_p$ , of  $p$  minus its  $\pi$ -electrons was determined by subtracting the number of electrons in the core and the number of electrons used to satisfy  $\sigma$ -valences of the neutral atom from the atomic number, e.g.,  $N_p$ (pyridine N) was taken as one while  $N_p$ (pyrrole N) and  $N_p$ (pyridinium N) was two.

Valence state ionization potentials and electron affinities were taken from Hinze and Jaffé [19] for the singly occupied orbitals of the atoms in a trigonal hybridization, e.g., 14.12 eV was taken as the ionization potential for all nitrogens, and 8.33 eV was taken for  $I_p$ (boron). Eq. (10) then gives  $H_{pp}$  values of  $-14.12$  eV,  $-26.46$  eV and  $-1.42$  eV for nitrogen with one  $\pi$ -electron, nitrogen with two  $\pi$ -electrons and boron with no  $\pi$ -electrons, respectively. For fluorine and chlorine these values were taken for the singly occupied  $p$  orbitals. The Pauling  $\sigma$ -orbital electronegativities used were also taken from Hinze and Jaffé [19]. The atomic parameters used are summarized in Table 1.

The effect of  $\sigma$ -polarization was introduced through Eqs. (11)–(13),

$$Z'_p = Z_p^0 + 0.35 \sum_q \left( \frac{2\chi_q}{\chi_p + \chi_q} - 1 \right) \left( \frac{1.41}{r_{pq}} \right)^2, \quad q \neq p, \quad (11)$$

$$I'_p = I_p^0 - 0.324 [(Z_p^0)^2 - (Z'_p)^2] - 6.03 [Z_p^0 - Z'_p], \quad (12)$$

$$\gamma'_{pp} = \gamma_{pp}^0 \left[ \frac{Z'_p}{Z_p^0} \right], \quad (13)$$

where  $Z_p^0$  is the Slater effective nuclear charge  $Z$ , computed using Slater's rules [20] for the atom without its  $\pi$ -electrons,  $Z'_p$  is the  $\sigma$ -corrected Slater  $Z$ , and  $r_{pq}$  is the internuclear separation between  $p$  and  $q$ . The factor, 0.35, is the Slater screening constant. The factor  $(1.41/r_{pq})^2$  is an arbitrarily chosen distance dependence for the  $\sigma$ -inductive effect. A factor of  $(1.41/r_{pq})^5$  was used to reduce the effect of distant atoms on the  $\sigma$ -correction but this did not alter the results appreciably. The constants in Eq. (12) are those computed by Warren and Yandle [21] for the iso-electronic series (C, N<sup>+</sup>, O<sup>++</sup>) and were used in the present calculations for all atoms. The initial SCF matrix was then computed using  $I'_p$  and  $\gamma'_{pp}$ .

Before each iteration a new Slater  $Z$ ,  $Z'_p$  was computed to account for variable  $\pi$ -charge densities [10],  $P_{pp}$ , according to Eq. (14),

$$Z''_p = Z'_p - 0.35 (P_{pp} - 1) \quad (14)$$

and  $I''_p$  and  $\gamma''_{pp}$  were then computed by equations analogous to Eqs. (12) and (13).

The electronic transitions were calculated from the ten lowest one-electron configurations by means of the configuration interaction routines in the original QCPE program. The molecular ionization potentials were obtained according to Koopmans [22].

### Discussion of Results

The results we have obtained with the above method are presented in Table 2 and Fig. 1. Wherever possible the calculated transitions were compared with the O-O band. Where measurements of the O-O band were lacking, the positions of these bands were estimated or the positions of maximum absorbance were used for the correlation, the difference between the O-O band and the absorbance maximum in most cases being no more than 0.2 eV.

The average deviations of the calculated from the observed values are 0.13 eV for transition energies and 0.4 eV for ionization potentials. These are smaller than the error in many of the experimental observations, and in some cases it is not known which is correct, calculation or observation. The predictions of ionization potentials by SCF-LCAO methods are often in error by 2 eV or more. It has been argued by Hoyland and Goodman [23] that this is due to the failure of Koopmans' theorem when the  $\Sigma$ - $\Pi$  separability condition is imposed.

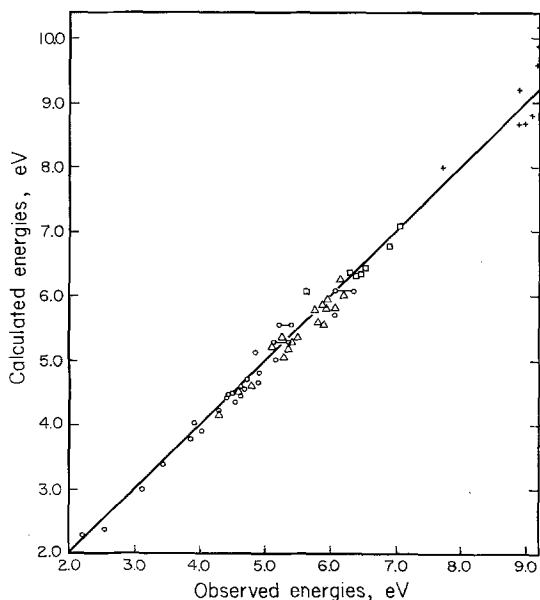


Fig. 1. Calculated transition energies and ionization potentials vs. observed: ○, first transition; △, second transition; □, third or higher transition; and +, ionization potential

Table 2. *Transition energies and molecular ionization potentials*


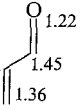



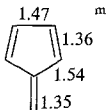

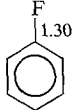
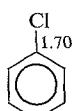
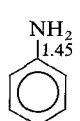
Molecule <sup>a</sup>	$\Delta E_i$ , eV		$f_i$ (or $\log \epsilon$ )		I.P., eV	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
	4.71 <sup>b</sup> 5.96 <sup>b</sup> 6.76 <sup>b</sup>	4.66 5.96 { 6.79 6.79	0.002 <sup>c</sup> 0.10 <sup>c</sup> 0.69 <sup>c</sup>	<10 <sup>-4</sup> <10 <sup>-4</sup> { 1.1 1.1	9.24 <sup>d</sup>	9.86
	6.39 <sup>e</sup> , 6.11 <sup>f</sup>	6.06	—	0.97	10.1 <sup>d</sup>	10.6
	5.2–5.4 <sup>g</sup> 5.88 <sup>h</sup>	5.56 5.86	(1.5) <sup>g</sup> (3.8) <sup>g</sup>	0.0005 0.25	9.0 <sup>f</sup>	8.7
	6.05 <sup>i</sup>	5.89 5.81	0.11 <sup>j</sup>	0.28 0.002	8.9 <sup>j</sup>	9.2
	5.13 <sup>k</sup> , 5.36 <sup>l</sup> 5.77 <sup>l</sup>	5.29 5.79	(3.9) <sup>l</sup> (3.8) <sup>l</sup>	0.01 0.34	8.9 <sup>k</sup>	8.7
	3.42 <sup>n</sup> 5.12 <sup>n</sup> —	3.39 5.25 6.24	0.012 <sup>n</sup> 0.032 <sup>n</sup> —	0.03 0.27 0.25	—	8.9
	4.9 <sup>f</sup> 6.2 <sup>f</sup> 6.9 <sup>f</sup>	4.66 6.01 6.76	0.04 <sup>f</sup> 0.10 <sup>f</sup> 1.3 <sup>f</sup>	0.01 0.004 1.0	9.2 <sup>d</sup>	10.2
	4.70 <sup>o</sup> 5.88 <sup>o</sup>	4.58 5.83	0.01 <sup>o</sup> —	0.01 0.05	9.2 <sup>p</sup>	9.4
	4.59 <sup>o</sup> 5.59 <sup>o</sup> 6.53 <sup>o</sup>	4.36 5.36 { 6.41 6.45	0.01 <sup>o</sup> (3.5) <sup>q</sup> (4.4) <sup>q</sup>	0.02 0.26 0.89 0.90	9.1 <sup>p</sup>	8.8
	4.3 <sup>r</sup> 5.3 <sup>r</sup> 6.45	4.20 5.06 { 6.29 6.39	0.03 <sup>r</sup> 0.17 <sup>r</sup> —	0.04 0.38 { 0.72 0.64	7.7 <sup>s</sup>	8.0

Table 2 (continued)

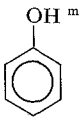
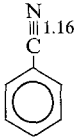
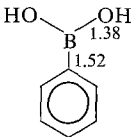
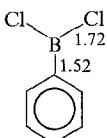
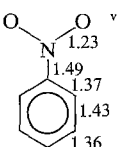
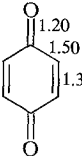
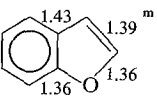
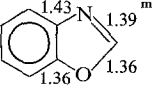
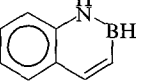
Molecule <sup>a</sup>	$\Delta E_i$ , eV		$f_i$ (or $\log \epsilon$ )		I.P., eV	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
	4.60 <sup>o</sup> 5.83 <sup>o</sup> 6.54 <sup>o</sup>	4.46 5.57 { 6.58 6.61	0.02 <sup>o</sup> 0.10 <sup>o</sup> 1.0 <sup>o</sup> 1.0 <sup>o</sup>	0.02 0.22 0.97 1.02	—	9.1
	4.49 <sup>q</sup> 5.4 <sup>q</sup> —	4.49 5.3 6.3	(2.8) <sup>q</sup> (4.0) <sup>q</sup> —	0.0004 0.68 0.76	—	9.5
	4.63 <sup>t</sup> 5.27 <sup>t</sup> 5.63 <sup>t</sup> 6.39 <sup>t</sup>	4.61 5.38 6.07 6.31	(2.8) <sup>t</sup> (3.5) <sup>t</sup> (4.0) <sup>t</sup> (4.7) <sup>t</sup>	0.006 0.42 0.18 0.38	—	10.0
	4.43 <sup>u</sup> —	4.49 5.01	— —	0.004 0.43	—	9.6
	— 4.9 <sup>q,w</sup> — 5.82 <sup>q</sup> 5.96 <sup>q</sup> 6.3 <sup>q</sup>	{ 4.66 4.83 5.14 5.60 5.95 6.35 6.40	— (3.8) <sup>q</sup> — (3.8) <sup>q</sup> (4.0) <sup>q</sup> (4.1) <sup>q</sup>	0.003 0.07 0.0003 0.30 0.007 0.40 0.93	—	9.3
	— 5.16 <sup>w</sup>	4.80 5.04	— (4.2) <sup>w</sup>	<10 <sup>-4</sup> 1.3	—	10.1
	4.41 <sup>x</sup> 5.12 <sup>x</sup> —	4.48 5.17 5.69	(3.5) (4.0) —	0.003 0.13 0.76	—	8.9
	4.49 <sup>y</sup> 5.37 <sup>y</sup>	4.35 4.88 5.49	(3.5) <sup>y</sup> (3.9) <sup>y</sup>	0.003 0.3 0.4	—	9.0
	3.90 <sup>z</sup> 4.59 <sup>z</sup> 5.45 <sup>z</sup>	4.02 4.52 5.15	— — —	0.10 0.15 0.53	—	9.2

Table 2 (continued)

Molecule <sup>a</sup>	$\Delta E_i$ , eV		$f_i$ (or $\log \epsilon$ )		I.P., eV	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
	3.85 <sup>aa</sup> 4.31 <sup>aa</sup> — 5.49 <sup>aa</sup>	3.78 4.19 5.20 5.32	(2.2) <sup>aa</sup> (3.5) <sup>aa</sup> — (4.9) <sup>aa</sup>	0.03 0.21 0.005 1.97	—	8.1
	3.12 <sup>cc</sup> — — —	3.02 4.08 4.55 4.88	— — — —	0.001 0.03 0.03 1.5	—	8.6
	3.1 <sup>dd</sup> 4.02 <sup>x</sup> 4.22 <sup>x</sup> 4.80 <sup>x</sup> —	— 3.90 4.62 4.71 5.30	— (3.2) <sup>x</sup> (3.6) <sup>x</sup> (4.9) <sup>x</sup> —	— 0.03 0.10 0.02 1.3	—	8.9
	2.53 <sup>ee</sup> —	2.36 <sup>ff</sup> 4.3 <sup>ff</sup>	— —	1.7 0.2	—	10.2
	2.22 <sup>ee</sup> —	2.15 <sup>ff</sup> 4.01 <sup>ff</sup>	— —	1.5 0.16	—	9.6
	4.85 <sup>gg</sup> 6.14 <sup>gg</sup>	5.17 6.26	— —	0.18 0.03	—	15.2

<sup>a</sup> Unless otherwise specified, all bond lengths are  $1.40 \pm 0.02$  Å and the bond length data are from Ref. [24].

<sup>b</sup> Parr, R. G.: J. chem. Physics **24**, 250 (1956).

<sup>c</sup> Clevens, H., Platt, J.: J. chem. Physics **17**, 470 (1949).

<sup>d</sup> Watanabe, K.: J. chem. Physics **26**, 542 (1957).

<sup>e</sup> Walsh, A. D.: Trans. Faraday Soc. **41**, 498 (1945).

<sup>f</sup> Ref. [26].

<sup>g</sup> Ref. [25].

<sup>h</sup> Pickett, L. W., Corning, M. E., Wieder, G. M., Semenow, D. A., Buckley, J. M.: J. Amer. chem. Soc. **75**, 1618 (1953).

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<sup>m</sup> Bond lengths estimated.

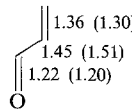
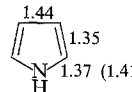
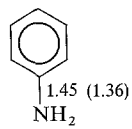
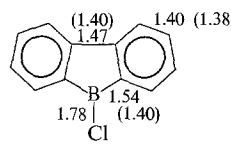
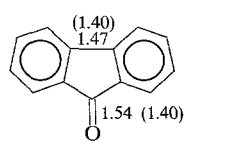
<sup>n</sup> Bloor, J. E., Gilson, B. R.: Theoret. chim. Acta (Berl.) **8**, 35 (1967).

<sup>o</sup> Ref. [14].



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- <sup>dd</sup> Ref. [27].
- <sup>ee</sup> West, W., Pearce, S., Grum, F.: J. physic. Chem. **71**, 1316 (1967); R = ethyl.
- <sup>ff</sup> R = hydrogen.
- <sup>gg</sup> Ref. [9].

Table 3. Effect of bond length variations on transition energies and oscillator strengths

Molecule	$\Delta E$ , eV	$f$
	6.06 (6.33) 7.28 (7.71)	0.97 (0.83) — (—)
	5.56 (5.56) 5.86 (5.73)	0.0005 (0.0005) 0.25 (0.26)
	4.20 (4.09) 5.06 (4.96) 6.29 (6.29) 6.39 (6.34)	0.04 (0.06) 0.38 (0.40) 0.72 (0.72) 0.64 (0.46)
	2.73 (2.40) 3.91 (3.81) 4.38 (4.28) 4.76 (4.68)	0.0003 (0.0008) 0.024 (0.008) 0.021 (0.016) 1.6 (1.7)
	3.56 (3.22) 4.43 (4.29) 4.56 (4.36) 5.13 (5.02)	0.03 (0.03) 0.04 (0.03) 0.02 (0.05) 1.4 (1.4)

The effect on calculated transition energies of variations in bond lengths was examined by computing several molecules using different structures, as shown in Table 3. It appears that small errors in a couple of bond lengths should not result in serious errors in the positions of the calculated energies, but some care should be taken to use realistic bond lengths. Thus, when fluorene-type bonds [24] were used for the bonds in B-chloroborfluorene, the lowest energy transition was predicted to be 0.4 eV lower than when the "correct" structure was used. When benzene bond lengths were used for all the bonds, the prediction was 0.3 eV lower still.

The calculations in Table 2 predict several  $\pi^* \leftarrow \pi$  transitions that have not been reported. In addition to all the bands of cyclopentadienone, they predict weak, long-wavelength bands for *p*-benzoquinone, nitrobenzene and benzoxazole. The weak, long-wavelength band recently reported by Mullen and Orloff [25] for pyrrole was not predicted by the method of Flurry *et al.* [26], but is predicted by this method. Also predicted are the higher energy transitions in B-chloroborfluorene.

The 3.1-eV band Yoshihara and Kearns [27] assigned as a  $\pi^* \leftarrow \pi$  transition in fluorenone is not predicted by our method when the bond lengths used are those of known fluorene derivatives (Table 2). The x-ray structure of fluorenone itself is unknown. If one uses benzene bonds for all the bonds in fluorenone (Table 3), a band is predicted at 3.2 eV, but there is no precedent for such short bonds in the five-membered rings of fluorene derivatives. The calculated and observed spectra of benzene, fulvene and *p*-benzoquinone, which contain the chromophores of fluorenone, are in good agreement. Thus, the assignment made by Yoshihara and Kearns is not verified by our method when reasonable bond lengths are used.

### Conclusions

The adjustment of atomic ionization potentials and repulsion integrals for  $\sigma$ -polarization effects and variable  $\pi$ -electronegativity in the SCF-MO-CI method permits the simultaneous prediction of electronic spectra and ionization potentials of heteroatomic molecules very reliably without using special empirical parameters. Small variations of the bond lengths used cause only small variations in predicted transition bands but care should be taken to obtain realistic bond lengths. When bond lengths from reported x-ray data on fluorene derivatives are used, the method fails to predict the weak 3.1-eV band assigned by Yoshihara and Kearns [27] as a  $\pi^* \leftarrow \pi$  transition in fluorenone.

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