L. C. B. O.: An Easy Method to Predict Valence Ionization Energies. Application to Substituted Benzenes

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The linear combination bond orbitals (L.C.B.O.) MO treatment has been used to reproduce the π ionization energies of several ortho-, meta- and para-disubstituted benzenes. The Coulomb integral of the substituent π orbitals and their resonance integrals with the ring π orbitals have been obtained from the spectra of the corresponding monosubstituted benzenes, using the same procedure for all the compounds under examination. The ring Coulomb integrals have been chosen taking, as an internal standard, the experimental ionization energy value of the $\pi(a_2)$ orbital, non interacting by symmetry in the monosubstituted and in the para-disubstituted compounds.

An application of this simple method to conformational analysis and to electron affinities is also shown.

Introduction

Photoelectron spectroscopy [1] provides the ionization energy values (IEs) related to atomic and molecular orbitals (AOs and MOs), measuring the kinetic energy of photoejected electrons: $IE_i = h\nu - KE_i$. In the approximation of the validity of Koopmans' theorem [2], IEs are equal to the negative orbital energies, $IE_i = -E_i$.

The development of this technique supplied a wealth of data on the electronic structure of molecular systems and also contributed to improve calculation methods providing empirical parameters and a test for their results. In turn, calculations provide a basis for the assignment of the bands of the photoelectron spectra to the corresponding MOs. Except for small molecules, even sophisticated calculation techniques often give energy values different from those experimentally determined. However, approximate MO methods of Hückel type can in many cases be employed successfully to predict valence ionization energies. Among these, the simplest is the L.C.B.O. method [3—6] (linear combination bond orbitals), which starts not from atomic orbitals but from the occupied group orbitals of the building blocks of a molecule, thus reducing the number of terms of the secular determinant. The agreement of the calculated energy levels with those experimentally determined is often as good as 0.1 eV. The MOs localization properties, with respect to the interacting group orbitals, are easily obtained as well, and the calculations can be performed with the only aid of a pocket calculator. For its simplicity, the L.C.B.O. method can easily be applied by experimentalists and can be useful in teaching the fundamentals of MO theory. In fact, it supplies a clear picture of the molecular orbital building-up.

The Hückel MO theory neglects the overlap integrals, so that $S_{ij} = \int \varphi_i \varphi_j \, \mathrm{d}v = 0$ unless $i = j$, and assumes that the integral $H_{ij} = \int \varphi_i h \varphi_j \, \mathrm{d}v$ is non zero only for adjacent atoms. The secular determinant for a linear system of interacting atomic orbitals, where the atomic orbitals are normalized and $S_{ij} = 1$,

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & \dots \\ H_{21} - ES_{21} & H_{22} - E & H_{23} - ES_{23} & \dots \\ \vdots & \vdots & \vdots & \end{vmatrix} = 0$$

becomes

$$\begin{vmatrix} H_{11} - E & H_{12} & 0 & \dots \\ H_{21} & H_{22} - E & H_{23} & \dots \\ \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \end{vmatrix} = 0,$$

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where the H integrals are called Coulomb integrals when $i=j$ and resonance integrals when $i \neq j$. In the LCAO approximation, the MOs of a polyene with N double bonds can be written as

$$\psi \equiv \sum_{\mu=1}^{2N} c_\mu \varphi_\mu$$

or, which is equivalent,

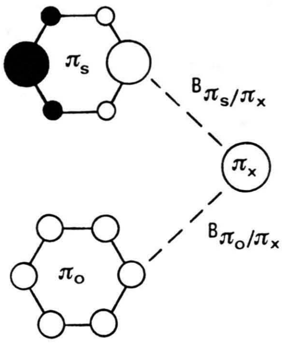
$$\psi \equiv \sum_{\mu=1}^{N} (c_\mu \pi_\mu + c_\mu{}^* \pi_\mu{}^*)$$

where π_μ and $\pi_\mu{}^*$ are the bonding and antibonding two centre orbitals of the double bond π_μ. The neglection of the interaction with the empty π^* orbitals ($c_\mu{}^* = 0$) leads to the L.C.B.O. model. The matrix elements are not mathematically evaluated but are empirical parameters which can compensate for the neglected integrals and the lack of empty orbitals. In particular, the numerical values, in units of energy, of the self energies (A) and of the interaction parameters (B) can be derived from the IEs of reference systems. Such a choice of the parameters takes therefore into partial account the non validity of Koopmans' theorem due to relaxation of the MOs under ionization and the correlation effects due to the mutually dependent electron motions.

Application of the L.C.B.O. Method to Substituted Benzenes

Let us consider first the π MOs of a benzene ring monosubstituted by a group (X) bringing an orbital of π symmetry (π_X): they derive from the interaction between the π_S and π_0 orbitals of the benzene fragment with the π_X orbital (see Figure 1). The π_A orbital does not mix with π_X, having a node on the carbon atom where X is attached. For the three interacting π group orbitals, belonging to the b_1 symmetry species in the C_{2v} point group, the secular determinant is:

$$\begin{vmatrix} A_{\pi_s} - E & B_{\pi_s/\pi_x} & 0 \\ B_{\pi_s/\pi_x} & A_{\pi_x} - E & B_{\pi_0/\pi_x} \\ 0 & B_{\pi_0/\pi_x} & A_{\pi_0} - E \end{vmatrix} = 0 .$$



Scheme I

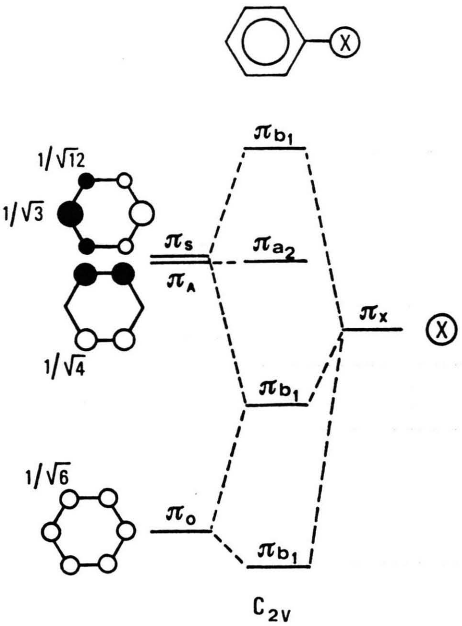


Fig. 1. Qualitative interaction diagram of the occupied π group orbitals of benzene and X substituent.

The determinant is a third power equation with respect to E, A_{π_s}, A_{π_0}, A_{π_x} and B_{π_s/π_x} being constant parameters. Being the resonance integral proportional to the size of the coefficients of the interacting orbitals, $B_{\pi_0/\pi_x} = B_{\pi_s/\pi_x} \times \sqrt{3/6}$. The fit of the calculated energies with the experimental values depends obviously on the choice of the basis set**.

In turn, the experimental energy values can be used to calculate unknown A and B parameters. For instance, the shift of the band related to photoejection from the not interacting π_A orbital in the photoelectron spectra of C_6H_5X with respect to benzene ($IE_{\pi_A} = IE_{\pi_s} = 9.24$ eV, $IE_{\pi_0} = 12.15$ eV)

** Once A, B and E values are known, from the secular equations

$$c_{\pi_s}(A_{\pi_s} - E) + c_{\pi_x} B_{\pi_s/\pi_x} = 0 ,$$
$$c_{\pi_s} B_{\pi_s/\pi_x} + c_{\pi_x}(A_{\pi_x} - E) + c_{\pi_0} B_{\pi_0/\pi_x} = 0 ,$$
$$c_{\pi_x} B_{\pi_0/\pi_x} + c_{\pi_0}(A_{\pi_0} - E) = 0 ,$$

and the normalization condition $c_{\pi_s}^2 + c_{\pi_x}^2 + c_{\pi_0}^2 = 1$, it is possible to calculate the sign and the size of the coefficients of the three MOs $\psi_i \equiv (c_{i\pi_s}\pi_S + c_{i\pi_x}\pi_X + c_{i\pi_0}\pi_0)$ with respect to the startin group orbitals.

provides an internal standard for the self energies A_{π_s} and A_{π_0}. This is done assuming that the three ring π orbitals are equally affected by the inductive effect of the substituent. A_{π_x} and B_{π_s/π_x} are still unknown but can be easily calculated from the secular determinant if two of the three energy levels, resulting from the interaction among π_S, π_X and π_0 are experimentally available.

For X=NH_2 [7], $N(CH_3)_2$ [7], OCH_3 [8], SCH_3 [8] and C≡CH [9], the following values for the Coulomb and resonance integrals are obtained:

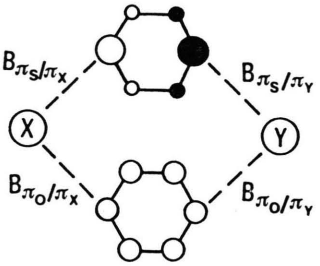
X	A_{π_x} (eV)	B_{π_s/π_x} (eV)
NH_2	− 10.29	− 1.45
$N(CH_3)_2$	− 8.53	− 1.19
OCH_3	− 10.81	− 1.33
SCH_3	− 9.12	− 1.05
C≡CH	− 10.68	− 1.065

For benzonitrile (X=CN), $A_{\pi_x} = -12.8$ eV [10] and $B_{\pi_s/\pi_x} = -0.96\sqrt{2/3}$ eV [11] have been reported.

In the following, these parameters are used to predict the π energy values of disubstituted benzenes. The photoelectron spectra of p-benzonitriles p-CN−C_6H_4−X (X=OCH_3, NH_2 and $N(CH_3)_2$ [12]) are reported in Figure 2. The IE of the second band provides the energy value for the self energies A_{π_s} and A_{π_0}, as described above.

The A_{π_x} values calculated for C_6H_5−X are shifted by 0.3 eV because of the strong electron withdrawing effect of the CN group (about 0.9 eV on the ring π_A orbital in C_6H_5−CN [10]). The following basis sets (values in eV) are obtained (Y=CN):

For the four $\pi(b_1)$ interacting group orbitals of X−C_6H_4−Y para-disubstituted benzenes (see scheme II)



Scheme II

the secular determinant is:

$$\begin{vmatrix} A_{\pi_x} - E & B_{\pi_s/\pi_x} & B_{\pi_0/\pi_x} & 0 \\ B_{\pi_s/\pi_x} & A_{\pi_s} - E & 0 & -B_{\pi_s/\pi_y} \\ B_{\pi_0/\pi_x} & 0 & A_{\pi_0} - E & B_{\pi_0/\pi_y} \\ 0 & -B_{\pi_s/\pi_y} & B_{\pi_0/\pi_y} & A_{\pi_y} - E \end{vmatrix} = 0\,.$$

The forth power equation gives the IE values reported in Fig. 2 as vertical bars, together with the experimental values. The wave function coefficients are given in Table 1.

The agreement with the experimental IE values ($IE_{\text{exp}} = 0.30 + 0.97\, IE_{\text{LCBO}}$; $r^2 = 0.998$) is so good that the two series of values are equal in the limits of the estimated experimental error (±0.05 eV). Therefore, the features appearing in the spectra in the energy region between π_3 and π_2 are assigned to ionization from σ orbitals.

X	A_{π_s}	A_{π_0}	A_{π_x}	A_{π_y}	B_{π_s/π_x}	B_{π_s/π_y}
OCH_3	− 9.97	− 12.85	− 11.1	− 12.8	− 1.33	$-0.96\sqrt{2/3}$
NH_2	− 9.85	− 12.75	− 10.6	− 12.8	− 1.45	$-0.96\sqrt{2/3}$
$N(CH_3)_2$	− 9.60	− 12.50	− 8.85	− 12.8	− 1.19	$-0.96\sqrt{2/3}$

An analogous calculation can be performed on the series p-X-C_6H_4−OCH_3 (X=NH_2, $N(CH_3)_2$, SCH_3 and OCH_3). The photoelectron spectra of these compounds [13] provide IE_{π_A}, from which A_{π_s} and A_{π_0} are evaluated. With the A_{π_x}, A_{π_y}, B_{π_s/π_x} and B_{π_s/π_y} values previously calculated from the spectra of the corresponding monosubstituted benzenes C_6H_5−X, the following basis sets (values in eV) are obtained (Y=OCH_3):

X	A_{π_s}	A_{π_0}	A_{π_x}	A_{π_y}	B_{π_s/π_x}	B_{π_s/π_y}
NH_2	− 9.15	− 12.05	− 10.29	− 10.81	− 1.45	− 1.33
$N(CH_3)_2$	− 9.03	− 11.95	− 8.53	− 10.81	− 1.19	− 1.33
SCH_3	− 9.26	− 12.15	− 9.12	− 10.81	− 1.05	− 1.33
OCH_3	− 9.24	− 12.15	− 10.81	− 10.81	− 1.33	− 1.33

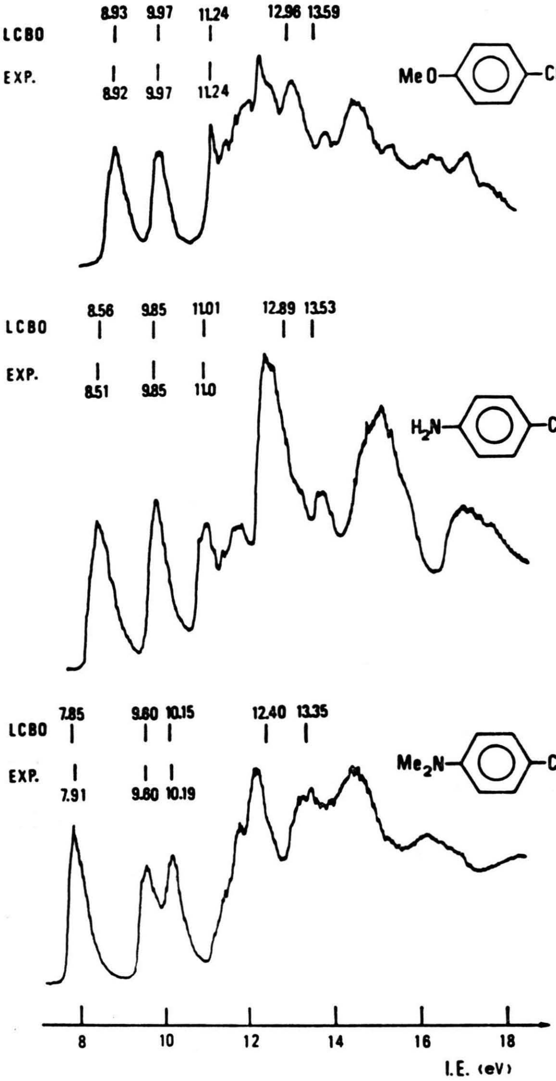


Fig. 2. Photoelectron spectra of para-substituted benzonitriles. Vertical bars are the experimental and calculated *IE* values.

Table 1. Wave function coefficients of the $\pi(b_1)$ MOs of p-$X{-}C_6H_4{-}CN$, in order of increasing ionization energy, with respect to the building group orbitals.

		π_X	π_S	π_O	π_{CN}
$X{=}OCH_3$	$\pi_4 \equiv$	0.547	− 0.815	− 0.110	− 0.155
	$\pi_3 \equiv$	0.638	0.426	− 0.508	0.392
	$\pi_2 \equiv$	0.461	0.391	0.358	− 0.711
	$\pi_1 \equiv$	0.287	− 0.015	0.780	0.555
$X{=}NH_2$	$\pi_4 \equiv$	0.613	− 0.768	− 0.133	− 0.131
	$\pi_3 \equiv$	0.610	0.510	− 0.478	0.373
	$\pi_2 \equiv$	0.434	0.386	0.423	− 0.696
	$\pi_1 \equiv$	0.250	− 0.030	0.757	0.603
$X{=}N(CH_3)_2$	$\pi_4 \equiv$	0.803	− 0.576	− 0.171	− 0.053
	$\pi_3 \equiv$	0.531	0.760	− 0.255	0.274
	$\pi_2 \equiv$	0.276	0.266	0.751	− 0.542
	$\pi_1 \equiv$	0.072	− 0.143	0.588	0.793

It is to be pointed out that for $Y{=}X{=}OCH_3$, because of the higher symmetry of the molecule, the 4×4 determinant can be substituted by two 2×2 determinants, thus simplifying the calculations. The out of phase combination of the oxygen lone pairs $n^- \equiv (\pi_X' - \pi_X'')/\sqrt{2}$ can interact only with π_S while the in phase combination ($n^+ \equiv (\pi_X' + \pi_X'')/\sqrt{2}$)only with π_O (see Figure 3). Being the two OCH_3 groups far from each other, the self energies A_{n^+} and A_{n^-} are degenerate and equal to A_{π_X}. The cross terms B_{n^+/π_O} and B_{n^-/π_S} are to be corrected taking into account the smaller ($1/\sqrt{2}$) coefficient at each oxygen atom and the doubled overlap with respect to the interaction of π_X with π_S and π_O in $C_6H_5{-}OCH_3$:

$$B_{n^+/\pi_O} = B_{\pi_X/\pi_O} \times 2/\sqrt{2};$$
$$B_{n^-/\pi_S} = B_{\pi_X/\pi_S} \times 2/\sqrt{2}.$$

The secular determinants

$$\begin{vmatrix} A_{\pi_S} - E & B_{n^-/\pi_S} \\ B_{n^-/\pi_S} & A_{n^-} - E \end{vmatrix} = 0$$

and

$$\begin{vmatrix} A_{n^+} - E & B_{n^+/\pi_O} \\ B_{n^+/\pi_O} & A_{\pi_O} - E \end{vmatrix} = 0$$

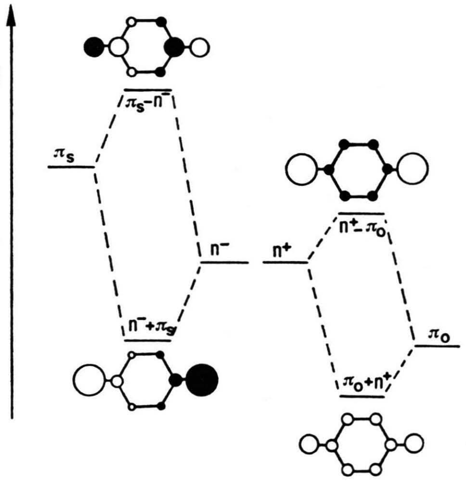


Fig. 3. Interaction diagram showing the symmetry allowed π interactions in p-$CH_3O{-}C_6H_4{-}OCH_3$.

Table 2. Calculated energies and experimental *IE*s for the π MOs of the series p-X$-C_6H_4-OCH_3$. Values are given in eV and *IE*s are taken from [12].

	E_{LCBO}	IE_{exp}		E_{LCBO}	E_{exp}
$X = NH_2$	-7.74	7.58	$X = SCH_3$	-7.82	7.80
	-9.15	9.15		-9.26	(8.72)[a]
	-9.73	10.00		-9.29	9.26
	-11.95	11.25 σ		-11.42	10.76 σ
		11.95			11.33
	-12.88			-12.81	
$X = N(CH_3)_2$	-7.31	7.18	$X = OCH_3$	-7.99	7.90
	-9.03	9.03		-9.24	9.24
	-9.01	9.26		-9.99	10.25
	-11.32	10.9 σ		-12.06	11.20 σ
		11.32			12.0
	-12.67			-12.97	

[a] This feature has been assigned to an impurity (see text).

lead to the following energies and parentages*:

$$E_4 = -\ 7.99\ \text{eV} \equiv 0.83\,\pi_S - 0.55\,n^-,$$
$$E_3 = -\ 9.99\ \text{eV} \equiv 0.85\,n^+ - 0.52\,\pi_0,$$
$$E_2 = -\,12.06\ \text{eV} \equiv 0.55\,\pi_S + 0.83\,n^-,$$
$$E_1 = -\,12.79\ \text{eV} \equiv 0.52\,n^+ + 0.85\,\pi_0.$$

The energy values calculated

$$(IE_{exp} = -0.12 + 1.01\,IE_{LCBO};\ r^2 = 0.993)$$

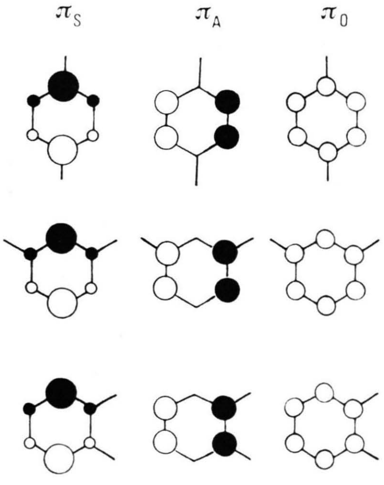
for the π orbitals (including π_A) of the series p-X$-C_6H_4-OCH_3$ are reported together with the experimental IEs in Table 2.

According to the calculated wave function coefficients, the highest occupied MO mainly derives from π_S when X=OCH_3 and NH_2, but from π_X when X=$N(CH_3)_2$. For X=SCH_3, the localization of the HOMO at the ring and at the substituents is almost the same.

One of the two experimental energy values reported in brackets in Table 2 is related to ionization from a σ orbital. These L.C.B.O. calculations indicate that the band at higher IE is always associated to the forth π orbital, in contrast with the assignment based on more sophisticated (CNDO/2) calculations [13]. The present result is in agreement with the qualitative expectation that the larger σ framework of the substituted benzenes has a lower IE onset than benzene (11.5 eV).

For X=SCH_3, the second experimental IE value (8.72 eV) has no counterpart in the calculations. We think that this band is due to the presence of $S(CH_3)_2$ impurity (*IE*=8.71 eV [14]) or of conformational isomers and that the second and third ionizations of p-$CH_3S-C_6H_4-OCH_3$ both contribute to the band peaking at 9.26 eV.

The B_{π_s/π_x} and A_{π_x} values obtained from ethynylbenzene ($C_6H_5-C\equiv CH$) are now emploied to perform L.C.B.O. calculations on the π system of ortho, meta and para-diethynylbenzenes, for which experimental *IE* values are available [4e]. The five group orbitals, from which the π MOs of these compounds originate, would lead to a 5 × 5 secular determinant. However, symmetry simplifications are possible. Scheme III shows the orientation of the substituents with respect to the nodal properties of the ring π orbitals.



Scheme III

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* For the π_S/n^- interaction, for example, the secular equation $c_{\pi_s}(A_{\pi_s} - E_i) + c_{n^-} B_{\pi_s/n^-} = 0$, with the normalization condition $c^2_{\pi_s} + c_{n^-} = 1$, gives: $c^2_{i\pi_s} = 1/1 + ((A_{\pi_s} - E_i)/B_{\pi_s/n^-})^2$ and $c_{in^-} = -c_{i\pi_s}(A_{\pi_s} - E_i)/B_{\pi_s/n^-}$.

In the para derivative, as seen for

$$\text{p-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3,$$

two 2×2 determinants are to be solved to account for the π_S/π_{cc}^- and π_0/π_{cc}^+ interactions, where the labels π_{cc}^- and π_{cc}^+ are related to the out of phase and to the in phase combinations of the acetylene π MOs, respectively. In the meta and ortho derivatives a 2×2 and a 3×3 determinant is needed, the symmetry allowed interactions being $\pi_S/\pi_{cc}^+/\pi_0$ and π_A/π_{cc}^- in the former, and $\pi_A/\pi_{cc}^+/\pi_0$ and π_S/π_{cc}^- in the latter. The experimental *IE* value (9.54 eV) of the non interacting π_A MO of p-diethynylbenzene leads to $A_{\pi_A} = A_{\pi_s} = -9.54$ eV and to $A_{\pi_0} = -12.45$ eV; with the previously calculated $A_{\pi_{cc}} = -10.68$ eV and $B_{\pi_s/\pi_{cc}} = -1.065$ eV, the following basis sets are obtained:

$$A_{\pi_A} = A_{\pi_s} = -9.54\ \text{eV};$$
$$A_{\pi_0} = -12.45\ \text{eV};$$
$$A_{\pi_{cc}^-} = A_{\pi_{cc}^+} = -10.68\ \text{eV}$$

for all the isomers.

p-diethynylbenzene:

$$B_{\pi_s/\pi_{cc}^-} = -1.065 \times \sqrt{2}\ \text{eV},$$
$$B_{\pi_A/\pi_{cc}^+} = B_{\pi_A/\pi_{cc}^-} = 0,$$
$$B_{\pi_0/\pi_{cc}^+} = -1.065\ \text{eV};$$

m-diethynylbenzene:

$$B_{\pi_s/\pi_{cc}^+} = -1.065 \times \sqrt{3/12} \times \sqrt{2}\ \text{eV},$$
$$B_{\pi_A/\pi_{cc}^-} = -1.065 \times \sqrt{3/4} \times \sqrt{2}\ \text{eV},$$
$$B_{\pi_0/\pi_{cc}^+} = -1.065 \times \sqrt{3/6} \times \sqrt{2}\ \text{eV};$$

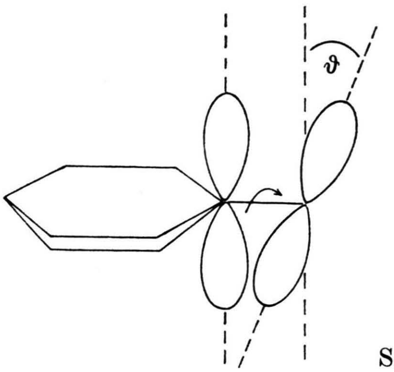
o-diethynylbenzene:

$$B_{\pi_s/\pi_{cc}^-} = -1.065 \times \sqrt{3/12} \times \sqrt{2}\ \text{eV},$$
$$B_{\pi_A/\pi_{cc}^+} = -1.065 \times \sqrt{3/4} \times \sqrt{2}\ \text{eV},$$
$$B_{\pi_0/\pi_{cc}^+} = -1.065 \times \sqrt{3/6} \times \sqrt{2}\ \text{eV}.$$

The calculated energy levels are reported in Table 3. They nicely fit the experimentally observed IEs and their trends

$$(IE_{\text{exp}} = 0.59 + 0.95\, IE_{\text{LCBO}};\ r^2 = 0.997).$$

The L.C.B.O. model, together with photoelectron spectroscopy data, can be emploied also for conformational analysis. Within the framework of a HMO-type model, the dependence of the interaction term B on the dihedral angle (ϑ) between the axis of the two interacting orbitals (see Scheme IV) is of the form: $B_\vartheta = B_0 \cos \vartheta$ [4a, 4f, 6b].



Scheme IV

As an example, we calculate the angle of rotation around the C—S bond in the sterically hindered $\text{C}_6\text{H}_5-\text{SB(n-Propyl)}_2$. The photoelectron spectrum of this molecule [15] gives the *IE* values 8.77 eV and 10.55 eV for the two outer $\pi(b_1)$ MOs resulting from the interaction among π_S, π_0 and π_X, where π_X refers to the sulphur lone pair, and 9.38 eV for π_A. From the 3×3 secular determinant, with $A_{\pi_s} = -9.38$ eV, $A_{\pi_0} = -12.29$ eV and the two above mentioned energy values, $A_{\pi_x} = -10.12$ eV and $B_{\pi_s/\pi_x} = -0.87$ eV are obtained.

The comparison of these data with those found for the coplanar thioanisole indicates that the higher ionization potential of the boron derivative is due to a) the stabilizing effect of boron, lowering the sulphur lone pair self energy and b) the reduced

Table 3. Calculated energies and experimental *IE*s for the π MOs of para-(D_{2h}), meta- and ortho- (C_{2v}) diethynylbenzenes. *IE*s are taken from [4e].

p-diethynylbenzene	E_{LCBO}	IE_{exp}
$2b_{2g}$ (π_s, π_{cc}^-)	− 8.50	8.58
$1b_{1g}$ (π_A)	− 9.54	9.54
$2b_{3u}$ (π_{cc}^+, π_0)	− 10.18	10.43
$1b_{2g}$ (π_s, π_{cc}^-)	− 11.72	11.74
$1b_{3u}$ (π_{cc}^+, π_0)	− 12.95	12.8
m-diethynylbenzene		
$2a_2$ (π_A, π_{cc}^-)	− 8.69	8.82
$3b_1$ (π_s, π_{cc}^+, π_0)	− 9.09	9.30
$2b_1$ (π_s, π_{cc}^+, π_0)	− 10.60	10.72
$1a_2$ (π_A, π_{cc}^-)	− 11.53	11.65
$1b_1$ (π_s, π_{cc}^+, π_0)	− 12.98	12.9
o-diethynylbenzene		
$3b_1$ (π_A, π_{cc}^+, π_0)	− 8.59	8.69
$2a_2$ (π_s, π_{cc}^-)	− 9.17	9.25
$2b_1$ (π_A, π_{cc}^+, π_0)	− 11.03	10.98
$1a_2$ (π_s, π_{cc}^-)	− 11.05	11.1
$1b_1$ (π_A, π_{cc}^+, π_0)	− 13.05	12.9

mixing between the sulphur lone pair and the ring π orbitals, due to rotation around the C—S bond. In particular, the ratio between the two resonance integrals gives

$$-0.87/-1.05 = \cos\vartheta; \quad \vartheta = 34°.$$

This result is close to that indicated by CNDO/2 calculations [15] for the smaller molecule C_6H_5—SBH_2 ($\approx 40°$). It has to be pointed out, however, that orbital interactions, not present in the coplanar conformer, can often arise in the rotated conformer. In the above example, we neglected the σ ring/π_x mixing which is non-zero when $\vartheta \neq 0°$. In a better approximation, we should have solved a 4×4 secular determinant, including in the basis set A_σ and $B_{\pi_x/\sigma} \cdot \cos(90° - \vartheta)$. This subject is dealt more extensively by Klessinger and Rademacher in reference [6b].

Application of the Method to the Unfilled Orbitals

The increasing availability of electron affinity (EA) data, obtained by means of Electron Transmission Spectroscopy [16] (ETS), stimulated us to test the applicability of this simple type of MO treatment to the empty orbitals. In fact, its success in predicting IE values does not necessarily imply its adequacy in predicting the energies of the shorter lived anion states formed for electron capture into unfilled MOs.

In this case, for analogy with the LCBO method, only interactions among group orbitals normally unoccupied are considered, neglecting their interaction with the filled orbitals. The empirical parameters A and B can be derived from the EA values of reference systems.

As an example, we calculate the energies of the empty orbitals of stilbene using parameters obtained from the ETS spectrum of styrene [17]. The procedure employed is the same as previously described for the filled orbitals. The used experimental data are the first three EA values of styrene (−0.25, −1.05 and −2.48 eV) and those of benzene (−1.12, doubly degenerate, and −4.82 eV [18]). The parameters $A_{\pi^*_{cc}} = 1.90$ eV and $B_{\pi^*_{cc}/\pi^*_s} = -1.10$ eV are obtained. Stilbene has seven π^* MOs. Three derive from the symmetry allowed interaction among π^*_{cc} with the out of phase combinations of the ring π^*_s and π^*_0 MOs (π^{*-}_s and π^{*-}_0). The remaining orbitals cannot interact by symmetry with the ethylene π^*_{cc} MO. Thus, the energy values of π^{*+}_s, π^{*+}_A, π^{*-}_A (nearly degenerate) and π^{*+}_0 are expected close to those of benzene.

The EA values of trans-stilbene, determined with ETS, are −0.97, −2.53, −4.4 and −5.0 eV [19]. On the basis of the above discussion, the features at 0.97 eV and 4.4 eV are related to the degenerate π^{*+}_s, π^{*+}_A and π^{*-}_A and to π^{*+}_0 MOs, respectively **. These two values are taken as Coulomb integrals for the π^{*-}_s and π^{*-}_0 orbitals. The basis set for the three orbital interaction is therefore

$$\begin{aligned} A_{\pi^{*-}_s} &= 0.97\ \text{eV}, & B_{\pi^{*-}_s/\pi^*_{cc}} &= -1.10\sqrt{2}\ \text{eV}, \\ A_{\pi^*_{cc}} &= 1.90\ \text{eV}, & B_{\pi^{*-}_0/\pi^*_{cc}} &= -1.10\ \text{eV}. \\ A_{\pi^{*-}_0} &= 4.4\ \text{eV}, & & \end{aligned}$$

The secular determinant leads to the following energy values (eV) for the three π^* MOs arising from the interaction among π^*_s, π^*_{cc} and π^*_0: −0.29, 2.65 and 4.91.

The calculated energies are in good agreement with those experimentally determined. In particular, the lowest unoccupied orbital is predicted to be stable and therefore not detectable by means of the ETS technique.

A good reproducibility of the EA values with this approach has also been found for other aromatic compounds [18].

** It can be observed that the π^{*+}_0 MO is stabilized with respect to the π^*_0 MO of benzene more than the π^{*+}_s MO with respect to the π^*_s MO of benzene. This finding is in line with what is observed in pyridines [18], benzaldehyde [18] and styrene [17], where the uppermost anion state is stabilized with respect to that of benzene, despite the destabilization caused by the substituent π^* orbital. It has been suggested [18] that this energy stabilization is due to the presence of doubly excited states at slightly higher energy.

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