Theoretical Study of Ionization Potentials in Monosubstituted Benzenes

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Abstract

Monosubstituted benzenes, in which the substituents participate in the π-electron system, are studied following a classification in two classes according to the π-electronic structure of the substituent. For this type of molecule, a relation is established between the nature of the substituent and, on the one hand, the energies of the two highest occupied molecular orbitals and, on the other hand, their respective differences. The two orbitals referred to above have π-character and belong to the a_2 and b_1 species if a C_{2v} point group is assumed. Simple symmetry arguments lead to the conclusion that the a_2 orbitals have, essentially, an intraring character, whereas the π-orbitals of the substituents do give an important contribution to the b_1 orbitals. Therefore, an a_2 electron must have a larger interaction with the benzene ring and a smaller kinetic energy, whereas a b_1 electron must have a larger interaction with the substituent and a larger kinetic energy. It is also expected that the changes in the π-electronic structure of the substituent must much more influence the variations on the b_1 energies and on the components of orbital energies associated with the substituent than the variations on the a_2 energies and on the intraring components of the orbital energies. A modified version of the MOPAC program was prepared to perform the decomposition of the orbital energies in their kinetic and potential energy components and these in their monocentric and bicentric terms. MNDO calculations on nine monosubstituted benzenes, using the modified MOPAC program, give good confirmation of the symmetry predictions and prove the consistency of the classification of the substituents that is introduced. © 1993 John Wiley & Sons, Inc.

I. Introduction

The values of many physicochemical properties of the substituted benzenes are markedly influenced by the nature of the substituent and several studies of this type of dependency can be found in the literature [1–13].

The purpose of this work is the theoretical study (within a semiempirical all-valence electron SCF formalism) of the influence of the nature of the substituent on the energies of the two highest occupied molecular orbitals of monosubstituted benzenes. The symmetry of these orbitals takes an important role in the discussion.

Two general types of effects (associated, respectively, with the π-electronic structure of the substituent and with the total charge transfer between the aromatic ring and the substituent) are used to classify the molecules and some effort is directed to situate them in the context of the classical effects used for this purpose.

The study of the influence that the nature of the substituent has in the form and energy of the two occupied molecular orbitals of highest energy has a special

interest for the understanding of the reactivity of substituted benzenes in electrophilic substitution reactions. Accepting as valid the charge-transfer mechanism proposed for this type of reaction [1, 12, 14–16], the first ionization potential (IP_1) of a molecule has been used as a reactivity index [1, 12], measuring the facility with which the molecule transfers electronic charge to the electrophile. On the other hand, Fukui et al. [17, 18], in their frontier orbitals theory, assumed that the position preferred for electrophilic substitution depends on the distribution of charge associated with the HOMO (highest occupied molecular orbital).

In this family of molecules, the two occupied molecular orbitals of highest energy have π-symmetry and, assuming the C_{2v} point group, they belong to the a_2 and b_1 species. Some theoretical studies have been presented aiming at a better understanding of the influence that the nature of the substituent has on the energy of these two orbitals.

Within a Hückel-type formalism, the influence of a substituent (X) in the energy of the above-mentioned molecular orbitals was studied [19] in terms of the inductive and resonance effects. The variation of the (electron-attracting or electron-donating) resonance action of the substituent X has been reflected in the formalism through an appropriate choice of the diagonal and nondiagonal elements of the Hückel matrix associated with X. The inductive action of X has been simulated by the change in the diagonal element of the Hückel matrix associated with the aromatic carbon adjacent to X and, in some cases, of the next-neighbor carbon atoms, as well.

Swain and Lupton [2], starting from the Hammett equations [20] as a base, suggested that certain properties (rate constants, equilibrium constants, ionization potentials, etc.) could be quantitatively written in terms of inductive and resonance parameters whose values depend on the nature of the substituent. The Hammett parameters have also been used in the calculations of ionization potentials on their own [5] or together with the coefficients of the respective molecular orbitals [11].

Godfrey [21, 22], using both the intermolecular charge transfer theory [23, 24] and the perturbation theory, introduced a semiempirical model in which the energy of the orbitals in question is correlated with parameters related with the π-inductive and the substituent charge-transfer effects. These parameters are calculated from spectroscopic data. The same type of data on monosubstituted benzenes has been frequently used in the parametrization of semiempirical methods to calculate ionization potentials in polysubstituted benzenes [25–27]. Several quantum mechanical methods have been used in this type of study, namely, PPP [27–31], HMO [25, 26, 29, 32], CNDO/S [33], SPINDO [34], LNDO/S [35], HAM/3 [36], and *ab initio* [6–10].

In this work, the effect of the substituent on the energy of the a_2 and b_1 orbitals of monosubstituted benzenes is analyzed using the decomposition of the orbital energy in its components, following its nature and location in terms of atomic centers. According to its nature, the orbital energies are partitioned in kinetic and potential components. According to location, the orbital energies are partitioned in monocentric and bicentric components and then grouped together in terms associated with the aromatic ring and the substituent.

Several energy partitioning schemes have been introduced: Kitaura and Morokuma [37] proposed a method to decompose the ab initio energy of interaction between two molecular systems in its components (electrostatic, polarization, exchange, charge

transfer, and coupling terms). This scheme was applied by Nagase et al. [38] in the study of strongly interacting systems. Other partitioning schemes were proposed for the SCF energy of a molecular system, within a semiempirical formalism (Fischer and Kollmar [39] and Dewar and Lo [40]) or an ab initio formalism (Kollmar [41]).

In this work, the orbital energies are subjected to a partitioning scheme similar to those proposed by Fischer and Kollmar [39] or Dewar and Lo [40] for the total energies. To gain a further understanding of the substituent effect, the separate partitioning of the kinetic and potential energies is attempted here.

In Section II, symmetry arguments are used to make a prediction of the influence of the π-electronic structure of the substituent on the values of the a_2 and b_1 orbital energies and their components. The results of the MNDO calculations for benzene and eight monosubstituted derivatives are presented in Section III. In Section IV, the validity of the symmetry predictions is discussed in great detail by comparison of the results of the molecular energy decomposition.

II. Symmetry Remarks and the Classification of the Substituents

In the substituted benzenes, several types of effects (inductive, resonance, charge transfer, etc.) have been used to classify the substituents. However, the different types of effects can be rearranged into two general types: the effects associated with π-electronic structure of the substituents and the effects associated with the total charge transfer between the aromatic ring and the substituents.

The π-electronic structure of the substituent conditions the form of the π-molecular orbitals of the substituted benzene and, consequently, the π-charge redistribution between the ring and the substituent. As the σ-charge transfer between the ring and the substituent usually dominates the total charge transfer between them, the second type of effects can be, reasonably, assumed to be independent of the first.

In this work, monosubstituted benzenes, in which the substituents participate in the ring's π-electron system, were studied. These are separated in two classes:

Class A: Those molecules in which the p_z orbital of the atom of the substituent adjacent to the ring is nonbonding.

Class B: Those molecules in which the p_z orbital of the atom of the substituent adjacent to the ring participates in the radical's π-electron system.

Four molecules of class A (fluorobenzene, phenol, methoxybenzene, and aniline) and four molecules of class B (benzaldehyde, nitrosobenzene, nitrobenzene, and cyanobenzene) were tested, and benzene were used for comparison. The present classification of the substituents studied coincides with that usually made in terms of the resonance effects, although a different criterion is used here. Indeed, class A of the present classification contains the electron-donating substituents by resonance effects, whereas class B contains the electron-accepting substituents by the same type of effects.

All the substituents studied are electron accepting when compared with hydrogen. However, the magnitude of the electron-accepting character of a substituent is not correlated with the class to which it belongs.

The two highest occupied molecular orbitals of benzene are degenerated and may be chosen as belonging to the b_1 and a_2 symmetry species. This choice is especially useful to understand the construction of the π-molecular orbitals when a hydrogen atom is substituted, producing a molecule with C_{2v} symmetry (approximate for some substituents and exact in other cases).

The atomic orbitals of the substituents do not give a significant contribution to the a_2 orbital as the substituted carbon (of the ring) is in a nodal plane (when the C_{2v} symmetry is assumed). On the other hand, these orbitals (when they have the appropriate symmetry) give an important contribution to the b_1 orbital.

Simple symmetry arguments may lead to the following statements:

1. The changes in the π-electronic structure of the substituent must more influence the variations on the b_1 orbital energies than the variations on the a_2 energies.

2. For all types of orbital energies (kinetic, potential, and total), the intraring component is always the largest because the a_2 orbitals localize almost all their electronic charge in the ring; this is still true for the b_1 orbitals but to a lesser extent. However, the components associated with the substituent may be important if one wishes to compare energies of an orbital in different molecules or energies of different orbitals in the same molecule.

3. An a_2 orbital has a nearly constant kinetic energy and, therefore, the variations on its total energy are almost entirely due to the variations on the potential energy component. A b_1 orbital of the same molecule has a larger kinetic energy because some amount of the π-charge is transferred from an atomic center (a carbon atom of the ring) where it is more contracted to another center [nitrogen, oxygen, or fluorine atom(s) of the substituent] where it is less contracted. This difference increases with the π-charge transferred and with the electronegativity of the above-mentioned centers of the substituent.

4. A b_1 electron has a larger interaction with the atomic cores of the substituent and a larger repulsion to their valence electrons than that of an a_2 electron of the same molecule.

5. An a_2 electron has a larger interaction with the cores of the atoms of the ring and a larger repulsion to their valence electrons than that of the b_1 electron of the same molecule.

6. The variations of the components of a b_1 potential energies associated with the substituent are more sensitive to the π-electronic structure of the substituent than to the total charge transfer between it and the ring, whereas the variations on the intraring component must reflect the two effects.

7. The variations of the ring-substituent components of the a_2 potential energies are more sensitive to the π-electronic structure of the substituent than to the total charge transfer between it and the ring, whereas this second type of effect must explain almost entirely the variations of the intraring component.

III. Calculations

In this work, the strategy followed in the discussion of the influence of the nature of the substituent on the first two ionization potentials of monosubstituted benzenes implies that the potential and kinetic orbital energies should be partitioned in monocentric and bicentric terms.

In the Appendix, a decomposition of this type is discussed in detail within the MNDO formalism [42]. A new subroutine is implemented in the MOPAC program [43] to perform this decomposition. The modified program is applied for the set of molecules considered here, the geometries being fully optimized from standard input geometries.

The basic common feature of the substituted benzenes that are studied here is the ring that, in this context, is taken as made up of six benzenoid carbon atoms and five hydrogens.

To allow a clearer discussion of the symmetry-based arguments, the orbital energy components described in detail in the Appendix may be used to make a separation of the orbital energy into contributions associated with the ring and the substituent. Let the a_2 or b_1 orbital energy, ε_i, be written as

$$\varepsilon_i = \varepsilon_i^r + \varepsilon_i^{r-s} + \varepsilon_i^s + \varepsilon_i^{\text{rem.}}, \tag{1}$$

where the four terms on the right-hand side have the following definitions:

ε_i^r is the intraring component of the orbital energy:

$$\varepsilon_i^r = \sum_{A\varepsilon\text{ring}} \varepsilon_i^A + \sum_{A<B\varepsilon\text{ring}} \varepsilon_i^{AB}. \tag{2}$$

ε_i^{r-s} contains the energy terms associated with the interaction between the ring and the atom (C) of the substituent adjacent to it:

$$\varepsilon_i^{r-s} = \sum_{A\varepsilon\text{ring}} \varepsilon_i^{AC}. \tag{3}$$

To simplify the notation, this component will be named the "ring-substituent component" as it includes most interactions of this type.

ε_i^s is the monocentric component of the orbital energy relatively to the atom(s) of the substituent that give(s) the largest contribution to the b_1 orbital. To simplify the notation, this component will be named the "intrasubstituent component" as it includes most interactions of this type.

$\varepsilon_i^{\text{rem}}$ is the remaining component of the orbital energy, including the components of interaction between the ring and the atoms of the substituent (excluding the one that is adjacent to the ring), the components of interaction among the atoms of the substituent, and the monocentric components relatively to the atoms of the substituent (excluding the one that gives the largest contribution to the b_1 orbital). Following the decomposition in the Appendix, each component (ε_i^x) of the orbital energy is partitioned in its potential and kinetic components:
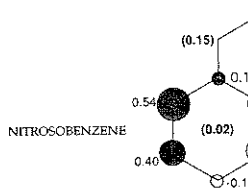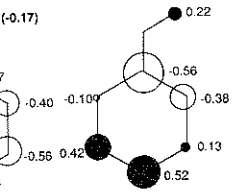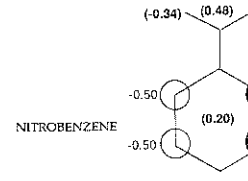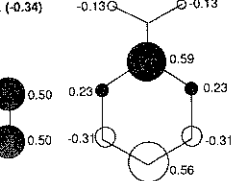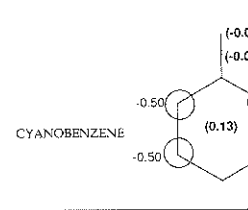
$$\varepsilon_i^x = V_i^x + T_i^x. \tag{4}$$

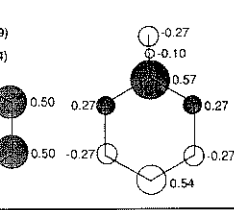$x = r$, $r - s$, s, or rem.

A description of the a_2 and b_1 molecular orbitals of the molecules considered is given in Table I (the coefficients) and Table II (the energetics). The first table contains also the net charges in the ring and in the atoms of the substituent.

TABLE I. Net charges (within brackets) and molecular orbitals coefficients of monosubstituted benzenes.

TABLE I. *(Continued)*

Molecule	a_2	b_1

An inspection of Tables III and IV allows a comparison between the experimental and the calculated ionization potentials. Given the variability of some experimental values, the agreement is very acceptable. In the molecules studied, the general trend observed for the calculated and experimental ε_{a_2} and ε_{b_1} values is almost the same.

IV. Discussion

The consistency of the classification of the substituents and the symmetry-based predictions can now be tested using the results of the MNDO calculations. The influence of the π-electronic structure of the substituent on the distribution of the a_2, b_1, and net charges between its atoms and the ring may be observed in Table I.

The anticipated nondirect correlation between the π-electronic structure of the substituent and the total charge transfer between the substituent and the ring is confirmed by the values of the ring's net charges, in the series of molecules studied. However, this structure has great influence in the intrasubstituent net charge distribution. In molecules of class A, the atom of the substituent adjacent to the ring has the largest electronegativity. This fact explains the large negative net charge of this atom. In substituents of class B, the above-mentioned atom is bonded to other more electronegative atom(s) of the substituent. This fact explains its less negative (usually positive) net charge, relatively to that in the molecules of class A. In benzene, the

TABLE II. The total energies and their components (in eV) for the a_2 and b_1 orbitals of monosubstituted benzenes.

		Intraring			Ring substituent			Intrasubstituent			Remaining			Total		
		V^r	T^r	ε^r	V^{r-s}	T^{r-s}	ε^{r-s}	V^s	T^s	ε^s	V^{rem}	T^{rem}	ε^{rem}	V	T	ε
Benzene	a_2	−51.46	42.36	−9.11	−0.28	0.00	−0.28	0.00	0.00	0.00	0.00	0.00	0.00	−51.75	42.36	−9.39
	b_1	−51.38	42.36	−9.03	−0.36	0.00	−0.36	0.00	0.00	0.00	0.00	0.00	0.00	−51.75	42.36	−9.39
Fluorobenzene	a_2	−52.82	42.38	−10.44	0.62	0.00	0.62	0.00	0.00	0.00	0.00	0.00	0.00	−52.20	42.38	−9.82
	b_1	−48.92	39.20	−9.72	1.51	−0.31	1.29	−7.37	6.42	−0.95	0.00	0.00	0.00	−54.78	45.31	−9.47
Phenol	a_2	−52.13	42.37	−9.78	1.01	−0.01	1.02	−0.03	0.03	0.00	−0.78	0.00	−0.78	−51.94	42.39	−9.55
	b_1	−44.75	36.44	−8.30	2.14	−0.44	1.70	−10.69	9.41	−1.29	−0.99	0.00	−0.99	−54.30	45.41	−8.88
Methoxybenzene	a_2	−52.48	42.35	−10.13	1.19	0.00	1.19	−0.03	0.03	0.00	−0.57	0.00	−0.57	−51.89	42.39	−9.50
	b_1	−44.24	35.88	−8.36	2.26	−0.43	1.83	−10.99	9.75	−1.24	−1.10	0.03	−1.07	−54.07	45.23	−8.83
Aniline	a_2	−51.84	42.38	−9.46	0.91	0.00	0.91	0.00	0.00	0.00	−0.91	0.00	−0.91	−51.84	42.38	−9.46
	b_1	−40.56	33.26	−7.30	1.94	−0.40	1.54	−10.49	8.91	−1.58	−2.13	0.72	−1.41	−51.24	42.49	−8.75
Benzaldehyde	a_2	−51.61	42.31	−9.30	−1.32	0.00	−1.32	−0.12	0.11	−0.01	0.91	0.00	0.91	−52.15	42.41	−9.74
	b_1	−49.00	40.31	−8.69	−1.48	−0.01	−1.48	−3.52	3.25	−0.27	0.61	0.04	0.65	−53.39	43.60	−9.79
Nitrosobenzene	a_2	−51.66	42.12	−9.54	−0.75	0.00	−0.75	−0.43	0.39	−0.04	0.49	0.00	0.49	−52.34	42.51	−9.82
	b_1	−49.03	40.15	−8.87	−1.01	0.02	−0.99	−3.82	3.49	−0.34	0.27	0.04	0.31	−53.59	43.70	−9.89
Nitrobenzene	a_2	−52.93	42.36	−10.57	−2.08	0.00	−2.08	0.00	0.00	0.00	2.34	0.00	2.34	−52.68	42.36	−10.31
	b_1	−50.95	40.84	−10.11	−2.28	−0.02	−2.30	−2.56	2.35	−0.21	2.06	0.08	2.14	−53.73	43.26	−10.48
Cyanobenzene	a_2	−52.58	42.37	−10.20	0.22	0.00	0.22	0.00	0.00	0.00	0.09	0.00	0.09	−52.26	42.37	−9.89
	b_1	−48.14	38.84	−9.30	0.66	−0.20	0.46	−4.10	3.72	−0.39	−1.25	0.67	−0.58	−52.83	43.01	−9.81

TABLE III.   The first ionization potential, in eV, of monosubstituted benzenes.

Molecule	IP$_1$					
	MNDO	Exp.[a]	Exp.[b]	Exp.[c]	Exp.[d]	Exp.[e]
Benzene	9.39	9.40	9.25	—	—	—
Fluorobenzene	9.47	9.50	9.30	—	—	—
Phenol	8.88	8.75	8.56	8.61	—	—
Methoxybenzene	8.83	8.54	—	8.39	8.45	—
Aniline	8.75	8.04	—	8.02	—	—
Benzaldehyde	9.74	9.80	—	9.57	—	9.59
Nitrosobenzene	9.82	9.97	—	—	—	—
Nitrobenzene	10.31	10.26	9.92	9.88	—	9.99
Cyanobenzene	9.81	10.02	9.71	9.79	—	9.73

[a][44].
[b][6, 7, 9, 10].
[c][45].
[d][46].
[e][47].

same situation occurs due to the electronic charge transfer from the hydrogen atom (less electronegative than a carbon atom) to the ring.

The distribution of the a_2 charge is not much influenced by the π-electronic structure of the substituent as almost all this charge is always localized in the ring. The distribution of the b_1 charge is significantly influenced by that structure. In fact, molecules of class A do normally localize a larger b_1 charge in the substituent than do molecules of class B. Moreover, in the first class, this charge is essentially localized in the atom of the substituent adjacent to the ring, the only one that has an occupied p_z orbital, whereas in the second class, this charge is localized, essentially, in the more electronegative atom(s) of the substituent that is(are) bonded to that atom. The symmetry-based predictions are consistent with these charge distributions and may be confirmed by inspection of Table II and Figures 1–6, as discussed below.

When the total orbital energies are compared for the nine molecules studied, it is clear that the variations among the a_2 orbitals are due to the variations on the potential energy component, the kinetic component being approximately constant (Fig. 1). For the b_1 orbital, a significant difference is found between the energy of class A and that of class B molecules (Fig. 2). This is due to a different degree of cancellation between the potential and kinetic energy terms with a very good compensation of the variations within each class.

A striking difference of behavior between class A and class B is also observed for the energy difference $(\varepsilon_{b_1} - \varepsilon_{a_2})$, as shown in Figure 3. In fact, this difference is markedly positive in class A (0.60 ±0.17eV), whereas for class B, it is very small indeed (−0.05 ±0.10 eV). This comes from the peculiar cancellation of the potential and kinetic energy components in a way similar to that mentioned above for the b_1 orbital.

TABLE IV.   The second ionization potential, in eV, of monosubstituted benzenes.

Molecule	IP$_2$					
	MNDO	Exp.[a]	Exp.[b]	Exp.[c]	Exp.[d]	Exp.[e]
Benzene	9.39	9.40	9.25	—	—	—
Fluorobenzene	9.82	9.86	9.88	—	—	—
Phenol	9.55	9.45	9.28	9.33	—	—
Methoxybenzene	9.50	9.37	—	9.22	9.25	—
Aniline	9.46	9.11	—	9.12	—	—
Benzaldehyde	9.79	9.80	—	9.75	—	9.81
Nitrosobenzene	9.89	9.97	—	—	—	—
Nitrobenzene	10.48	10.26	9.92	9.88	—	10.35
Cyanobenzene	9.89	10.02	10.12	10.11	—	10.15

[a] [44].
[b] [6, 7, 9, 10].
[c] [45].
[d] [46].
[e] [47].

The b_1 orbitals always have larger kinetic energies than those of the a_2 orbitals (Fig. 3). This is due to the positive values of $T_{b_1}^s$ ($T_{a_2}^s \approx 0$) that dominate the negative differences ($T_{b_1}^r - T_{a_2}^r$).

For all types of orbital energies (total, potential, and kinetic), the intraring component is always the most important, this tendency being more striking for the a_2 orbital.
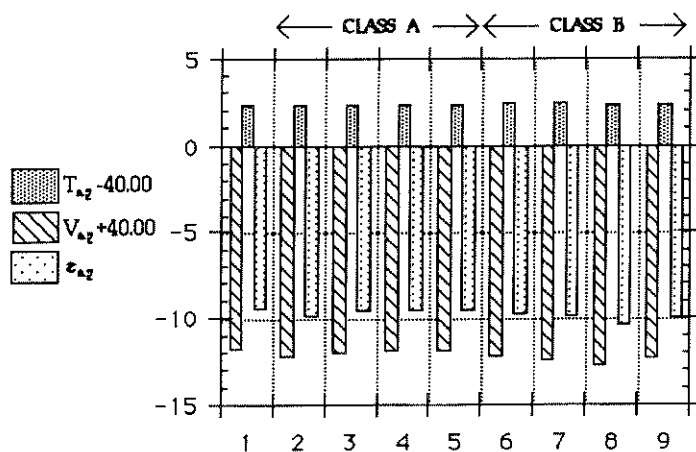

Figure 1.   The total energy and its components, in eV, for the a_1 molecular orbital of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.
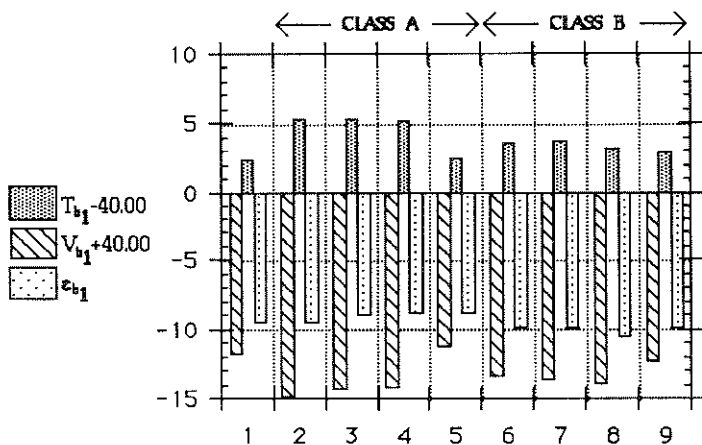
Figure 2. The total energy and its components, in eV, for the b_1 molecular orbital of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.

A b_1 orbital has a larger absolute value of the potential ring-substituent energy, V^{r-s}, and a larger negative intrasubstituent potential energy, V^s, than those of an a_2 orbital of the same molecule (Fig. 4 and Table II). This is consistent with a b_1 electron having a larger interaction with the substituent than that of an a_2 electron. An a_2 orbital has a larger negative value of the intraring potential energy, V^r, than that of a b_1 orbital of the same molecule (Fig. 4), which is consistent with an a_2 electron having a larger interaction with the ring than that of a b_1 electron.
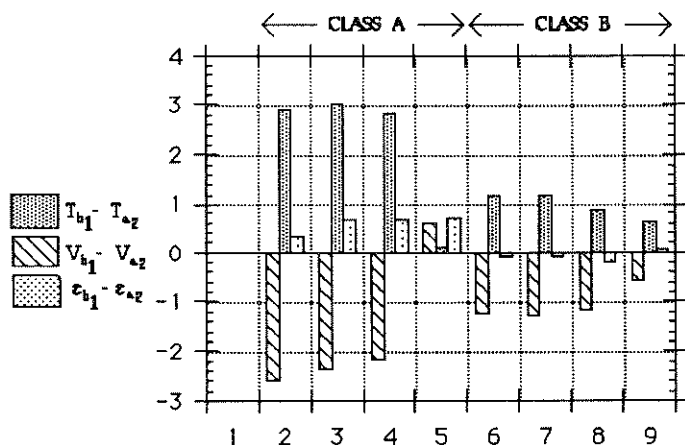

Figure 3. Energy difference between the b_1 and a_2 molecular orbitals and its components, in eV, of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.
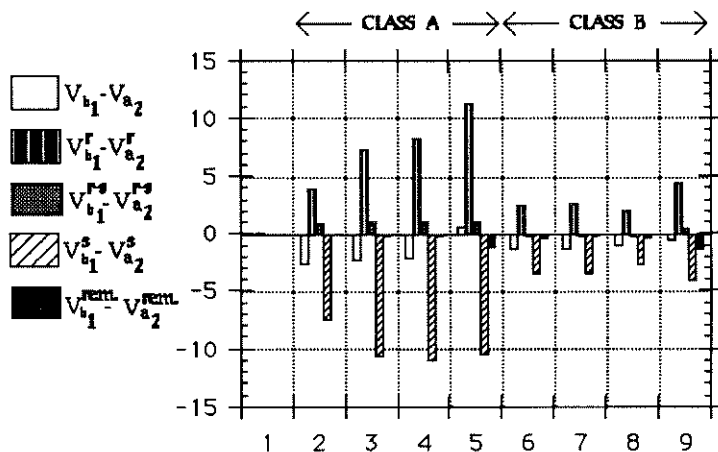
Figure 4. Potential energy difference between the b_1 and a_2 molecular orbitals and its components in eV, of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.

The differences of potential energies between the b_1 and a_2 orbitals of the same molecule $(V_{b_1} - V_{a_2})$ are, usually, negative (Fig. 4) due to the negative values of $V_{b_1}^s$ $(V_{a_2}^s \approx 0)$ that dominate the positive values of $(V_{b_1}^r - V_{a_2}^r)$. Aniline is the only exception due to the large b_1 charge transfer from the ring to the nitrogen atom that has a small difference of electronegativity relatively to a carbon atom.

The intraring potential energy of a b_1 orbital, $V_{b_1}^r$, is conditioned by the total and by the b_1 charge localized in the ring. Therefore, its variation (Fig. 5) along the
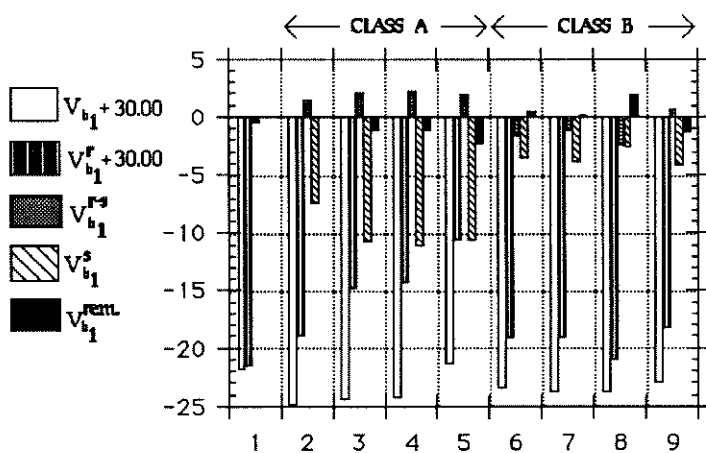

Figure 5. The potential energy and its components, in eV, for the b_1 molecular orbital of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.

Figure 6.   The potential energy and its components, in eV, for the a_2 molecular orbital of monosubstituted benzenes. 1. Benzene; 2. fluorobenzene; 3. phenol; 4. methoxybenzene; 5. aniline; 6. benzaldehyde; 7. nitrosobenzene; 8. nitrobenzene; 9. cyanobenzene.
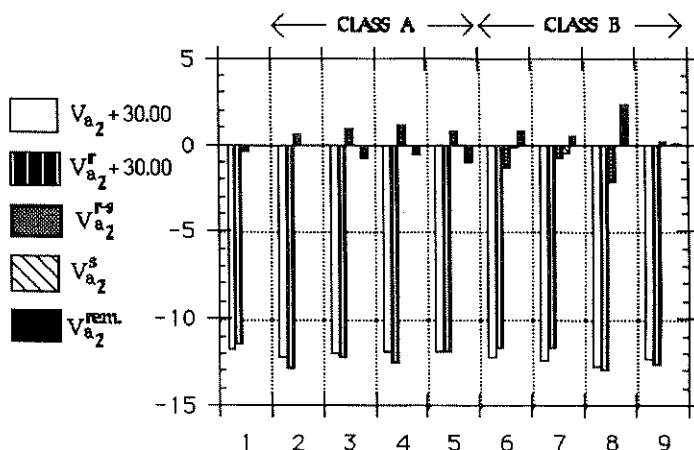
series of the molecules studied is conditioned by both the π-electronic structure of the substituent and the total charge transfer between the substituent and the ring. The same energetic component of an a_2 orbital, $V_{a_2}^r$, is almost completely conditioned by the above-mentioned total charge transfer and is quite independent of the π-electronic structure of the substituent (Fig. 6).

The intrasubstituent potential energy of a b_1 orbital, $V_{b_1}^s$, is always negative (Fig. 5) because the core of the atom of the substituent associated to this component is more efficient at interacting with the b_1 charge localized in the same atom than its remaining charge. This efficiency must increase when the electronegativity of this atom increases. Therefore, $V_{b_1}^s$ decreases with the increase of the mentioned electronegativity and with the increase of the b_1 charge localized in this same atom. In fact, their values are more negative in the molecules of class A than in the molecules of class B, which is consistent with the different degree of localization of the b_1 charge between the two classes. The intrasubstituent potential energy of an a_2 orbital, $V_{a_2}^s$, is always close to zero (Fig. 6) due to the almost null a_2 charge localized in the substituent.

The ring-substituent energies of the b_1 and a_2 orbitals, $V_{b_1}^{r-s}$ and $V_{a_2}^{r-s}$, are very sensitive the π-electronic structure of the substituent (Figs. 5 and 6). Indeed, their values are strikingly positive for the molecules of class A and much smaller (usually negative) for the molecules of class B and for benzene. These results are in agreement with the different distributions of the net and orbital charges among the atoms of the substituent, in the two classes of molecules.

Several points of convergence exist between the present theory of substituent effects developed within a semiempirical all-valence electron SCF formalism and the classical theory (built around the concepts of inductive and resonance effects) rationalized within a Hückel-type formalism [19]:

(a) Two general types of substituent effects are considered upon the orbital energies, namely, σ-electronic effects and π-electronic effects. The first ones are essentially associated with the intraring component of the orbital energies. The π-electronic effects are essentially associated with the components of orbital energy that involve the substituent.

(b) The classification of the substituents made in terms of π-electronic effects now proposed coincides with the classical classification in terms of resonance effects.

(c) The major variations of the orbital energies are associated with π-electronic effects. Indeed, the most usual heteroatom parametrizations [19] neglect the inductive effect relatively to the resonance effect, and in the present SCF calculations, it can be emphasized that the variations on the b_1 energies (which can be mostly associated with the π-electronic structure of the substituent) are far more important than the variations on the a_2 energies (which can be mostly associated with charge-transfer effects).

One peculiarity of this work is the separate analysis of the kinetic and potential orbital energies. This partitioning allows a clear justification of some results initially established on simple symmetry arguments:

When a π-molecular orbital of a monosubstituted benzene presents a large charge localization in the aromatic ring (the a_2 orbital, e.g.), its kinetic energy is nearly constant and its potential energy has small changes due mainly to charge-transfer effects. The delocalization of charge to the substituent (as in the b_1 orbital) leads to great variations in these two components of the orbital energy. These variations are usually in the opposite sense and their degree of cancellation is essentially dependent on the π-electronic structure of the substituent. In the molecules of class B (electron-accepting electrons by the resonance effect in the classical theory), this compensation is very good and the orbital energy difference $(\varepsilon_{b_1} - \varepsilon_{a_2})$ is close to zero. In the molecules of class B (electron-donating electrons by the resonance effect in the classical theory), this compensation is not so good and the above-mentioned difference is markedly positive.

The following conclusions may be drawn from the results presented in this paper:

1. The two features (total charge transfer between the ring and the substituent and π-electronic structure of the substituent) that are assumed to influence the energy of the b_1 and a_2 orbitals of monosubstituted benzenes are reasonably independent and the major variations on the orbital energy are associated with the second feature.

2. The components of the orbital energies associated with the substituent are more sensitive to the changes in the π-electronic structure of the substituent than are the intraring components of the orbital energies.

3. A localization of orbital charge in the ring (as in the a_2 orbital, e.g.) is associated with a constant kinetic energy and with small variations in potential energy. A delocalization of charge to the substituent (as in the b_1 orbital) leads to great variations in these two components, usually in the opposite sense, and the degree of compensation between them is essentially dependent on the π-electronic structure of the substituent.

V. Appendix: Decomposition of the Orbital Energy

The MNDO energy (ε_i) of orbital ψ_i of a molecular system can be broken into monocentric and bicentric contributions [42]:

$$\varepsilon_i = \sum_A \varepsilon_i^A + \sum_{A<B} \varepsilon_i^{AB}. \tag{A1}$$

The monocentric (ε_i^A) and bicentric (ε_i^{AB}) terms can, in turn, be also partitioned into their components:

$$\varepsilon_i^A = U_i^A + {}^R V_i^A = T_i^A + {}^C V_i^A + {}^R V_i^A \tag{A2}$$

$$\varepsilon_i^{AB} = \beta_i^{AB} + {}^C V_i^{AB} + {}^R V_i^{AB} = T_i^{AB} + {}^\beta V_i^{AB} + {}^C V_i^{AB} + {}^R V_i^{AB}. \tag{A3}$$

The energy component U_i^A is the monoelectronic, monocentric energy of ψ_i associated with atom A and may be calculated by the expression

$$U_i^A = \sum_{p\varepsilon A} c_{pi}^* c_{pi} \langle \chi_p(1) | -\frac{1}{2} \nabla_1^2 - V_A(1) | \chi_p(1) \rangle = \sum_{p\varepsilon A} c_{pi}^* c_{pi} h_{pp}, \tag{A4}$$

where $-V_A(1)$ is the potential energy of interaction between electron 1 and the core of atom A, c_{pi} is the contribution of the atomic orbital χ_p to the molecular orbital ψ_i, and the sum is extended over all valence orbitals of this atom.

U_i^A can be further decomposed into its kinetic (T_i^A) and potential $({}^C V_i^A)$ energy components: T_i^A represents the contribution of the charge of ψ_i localized in A to the kinetic energy of this orbital, given by the expression

$$T_i^A = \sum_{p\varepsilon A} c_{pi}^* c_{pi} \langle \chi_p(1) | -\frac{1}{2} \nabla_1^2 | \chi_p(1) \rangle = \sum_{p\varepsilon A} c_{pi}^* c_{pi} T_{pp}, \tag{A5}$$

and ${}^C V_i^A$ is the contribution for the potential energy of ψ_i given by the attraction between its charge localized in A and the core of this atom, calculated by the expression

$$^C V_i^A = \sum_{p\varepsilon A} c_{pi}^* c_{pi} \langle \chi_p(1) | -V_A(1) | \chi_p(1) \rangle = \sum_{p\varepsilon A} c_{pi}^* c_{pi} {}^C V_{pp}. \tag{A6}$$

${}^R V_i^A$, in eq. (A2), is the contribution to the potential energy of ψ_i given by the interaction between its charge localized in A and the remaining electronic charge of this atom:

$$^R V_i^A = \sum_{p\varepsilon A} \sum_{r\varepsilon A} P_{rr} c_{pi}^* c_{pi} \left[(pr \mid pr) - \frac{1}{2} (pp \mid rr) \right]$$

$$+ \sum_{p\varepsilon A} \sum_{r \neq p\varepsilon A} P_{pr} c_{pi}^* c_{ri} \left\{ \frac{3}{2} (pp \mid rr) - \frac{1}{2} (pr \mid pr) \right\}, \tag{A7}$$

where P_{pr} is the density matrix element associated with atomic orbitals χ_p and χ_r:

$$P_{pr} = 2 \sum_j c_{pj}^* c_{rj}, \tag{A8}$$

with the sum extended over all the occupied molecular orbitals, and $(pq \mid rs)$ is the bielectronic integral associated with atomic orbitals χ_p, χ_q, χ_r, and χ_s:

$$(pq \mid rs) = \langle \chi_p(1)\chi_q(2)|1/r_{12}|\chi_r(1)\chi_s(2)\rangle. \tag{A9}$$

β_i^{AB}, in eq. (A3), is the resonance energy of ψ_i, relative to atoms A and B:

$$
\begin{aligned}
\beta_i^{AB} &= 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \left\langle \chi_p(1)\left| -\frac{1}{2}\nabla_1^2 - V_A(1) - V_B(1)\right|\chi_r(1)\right\rangle \\
&= 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \beta_{pr}.
\end{aligned} \tag{A10}
$$

β_i^{AB} can be decomposed in its kinetic (T_i^{AB}) and potential ($^\beta V_i^{AB}$) components: T_i^{AB} is the contribution to the kinetic energy of ψ_i that is given by the electronic charge of overlap between A and B:

$$T_i^{AB} = 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \left\langle \chi_p(1)\left| -\frac{1}{2}\nabla_1^2\right|\chi_r(1)\right\rangle = 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} T_{pr}. \tag{A11}$$

and $^\beta V_i^{AB}$ is the contribution to the potential energy of ψ_i that is given by the attraction between its electronic charge of overlap between A and B and the cores of these atoms:

$$^\beta V_i^{AB} = 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \langle \chi_p(1)|-V_A(1) - V_B(1)|\chi_r(1)\rangle = 2 \sum_{p\varepsilon A} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \,^\beta V_{pr}. \tag{A12}$$

$^C V_i^{AB}$, in eq. (A3), is the contribution to the potential energy of ψ_i given by the attraction between its electronic charge localized in B and the core of A and vice versa:

$$^C V_i^{AB} = \sum_{p\varepsilon A} \sum_{r\varepsilon A} c_{pi}^* c_{ri} \,^C V_{pr}^B + \sum_{p\varepsilon B} \sum_{r\varepsilon B} c_{pi}^* c_{ri} \,^C V_{pr}^A, \tag{A13}$$

with

$$^C V_{pr}^B = \langle \chi_p(1)|-V_B(1)|\chi_r(1)\rangle \tag{A14}$$

and

$$^C V_{pr}^A = \langle \chi_p(1)|-V_A(1)|\chi_r(1)\rangle. \tag{A15}$$

$^R V_i^A$, in eq. (A3), is the contribution to the potential energy of ψ_i, given by the interaction between its electronic charge localized in A and the remaining electronic charge in B and vice versa:

$$
\begin{aligned}
^R V_i^{AB} = &\sum_{p\varepsilon A} \sum_{r\varepsilon A} \sum_{q\varepsilon B} \sum_{s\varepsilon B} P_{qs} c_{pi}^* c_{ri}(pq \mid rs) + \sum_{p\varepsilon B} \sum_{r\varepsilon B} \sum_{q\varepsilon A} \sum_{s\varepsilon A} P_{qs} c_{pi}^* c_{ri}(pq \mid rs) \\
&- \frac{1}{2} \sum_{p\varepsilon A} \sum_{s\varepsilon A} \sum_{q\varepsilon B} \sum_{r\varepsilon B} P_{qs} c_{pi}^* c_{ri}(pq \mid sr) \\
&- \frac{1}{2} \sum_{p\varepsilon B} \sum_{s\varepsilon B} \sum_{q\varepsilon A} \sum_{r\varepsilon A} P_{qs} c_{pi}^* c_{ri}(pq \mid sr). \tag{A16}
\end{aligned}
$$

TABLE V.   Monocentric monoelectronic integrals for atoms of the second period.

Atom	$T_{pz,pz}$ (eV)	$-V_{pz,pz}$ (eV)	$\lvert T_{pz,pz}/V_{pz,pz}\rvert$
C	40.211	79.420	0.506
N	51.685	109.040	0.474
O	68.811	146.719	0.469
F	88.384	194.251	0.455

In the MNDO method, the basis of atomic orbitals includes all the valence orbitals of the occupied levels in each atom. Internal electrons are absorbed with the nuclear charge into an atomic core. The valence atomic orbitals of the basis set are formally approximated by Slater-type orbitals (STO) with exponents (ζ) assumed to be variationally optimized. These functions used explicitly only to evaluate the total resonance integrals (β_{pr}) and their ζ exponents do not have a physical meaning out of this context.

In a conventional MNDO calculation, the h_{pp} and β_{pr} integrals are not decomposed in their potential and kinetic components ($^{C}V_{pp}$ and T_{pp}, and, $^{\beta}V_{pr}$ and T_{pr}, respectively). As this decomposition was required for our analysis, one of the components had to be evaluated analytically and the other calculated by difference to the total integral (h_{pp} or β_{pr}).

The analytical evaluation of the potential integrals causes some problems as it requires an explicit form for the core operators V_A. To avoid this difficulty, the kinetic integrals were evaluated analytically, whereas the potential integrals were calculated by the difference. The selection of the functions to approximate the atomic orbitals in these calculations is the only problem that remains.

The Slater-type orbitals, with the exponents of MNDO parametrizations, can give good results for the monocentric and resonance energy components in the semiempirical formalism used, but they are not likely to be good functions for the present calculation. In this work, an STO minimal basis with the optimized exponents proposed by Hehre et al. [48] is used to represent the atomic orbitals and it is reasonable to expect more consistent results with this basis than with the previous one. The kinetic resonance integrals (T_{pr}) are calculated by the formula given by Roothaan [49].

The values of the $T_{p_z p_z}$ integrals (analytically evaluated by the above-mentioned procedure) and of the $V_{p_z p_z}$ integrals (calculated by difference between $h_{p_z p_z}$ and $T_{p_z p_z}$) are given in the Table V.

The absolute values of $V_{p_z p_z}$ and $T_{p_z p_z}$ increase as the atomic number increases, which is consistent with, respectively, the increase of the core charge and the decrease of the atomic radius (increase of the p_z electron constrictions).

The absolute value of the ratio ($T_{p_z p_z}/V_{p_z p_z}$) decreases as the atomic number increases, which is consistent with the increase of the ionization potential.

The results of this Appendix are used in the text.

Acknowledgment

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