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A SIMPLE ALGORITHM FOR THE CALCULATION OF THE π IONIZATION ENERGIES OF SUBSTITUTED BENZENES

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Abstract - A simple algorithm, based on HMO approach is used for calculating π-ionization potentials (π-IP's) of polysubstituted benzenes. The parameters required for the method are determined from π-IP's of monosubstituted benzenes. For 50 disubstituted benzenes the first three values of the π-IP's are obtained with root mean square (rms) error of 0.19 eV. Some examples of application are presented, illustrating the possibility of fast and quite accurate estimation of π-IP's for polysubstituted benzenes.

INTRODUCTION

The development of photoelectron spectroscopy makes it possible to determine ionization potentials (IP's) with considerable accuracy. This stimulates the growth of the need to predict the IP's using theoretical methods. The ability of making such predictions plays a central role in several branches of chemistry, for instance in the theory of the EDA complexes[1] and pericyclic reactions.[2] However, it was found, that the application of the more sophisticated ZDO methods, like CNDO/S[3], MNDO[4], SPINDO[5], LNDO/S[6] or HAM/3[7] often gives results not as good as those obtained in simple approaches such as HMO[8] or LCBO[9]. The results of ab initio calculations, especially of the double zeta ones, are often very close to the experimental data [10-14], but unfortunately require a lot of computational time and extremely large storage for the electron-electron repulsion integrals. Therefore they become impractical as a routine treatment for large molecules.

Although there are a number of papers concering various approaches to calculating the π-IP's based on HMO and/or LCBO methods[8,9,15] it seems, that such a treatment is seldom used by organic chemists. The purpose of this paper is to show, how reliable values of π-ionization potentials can be obtained using a simple and computationally very efficient method and at the same time re-emphasise the advantages of the HMO approach in calculations of this type. The algorithm given together with the parameters determined for some common substituents can serve as a practical tool for the interpretation of PE spectra of various polysubstituted benzenes and play a similar role to the additive increment schemes in calculations of the chemical schift in NMR-spectroscopy. An interactive FORTRAN program (Fig.1), available upon request, can be readily adapted for microcomputers or home computers or even coded in the pocket calculator. Therefore the method presented, even if it has no well established quantum-mechanical foundations, could be used as a simple means of estimating π-IP's in organic chemistry laboratories.

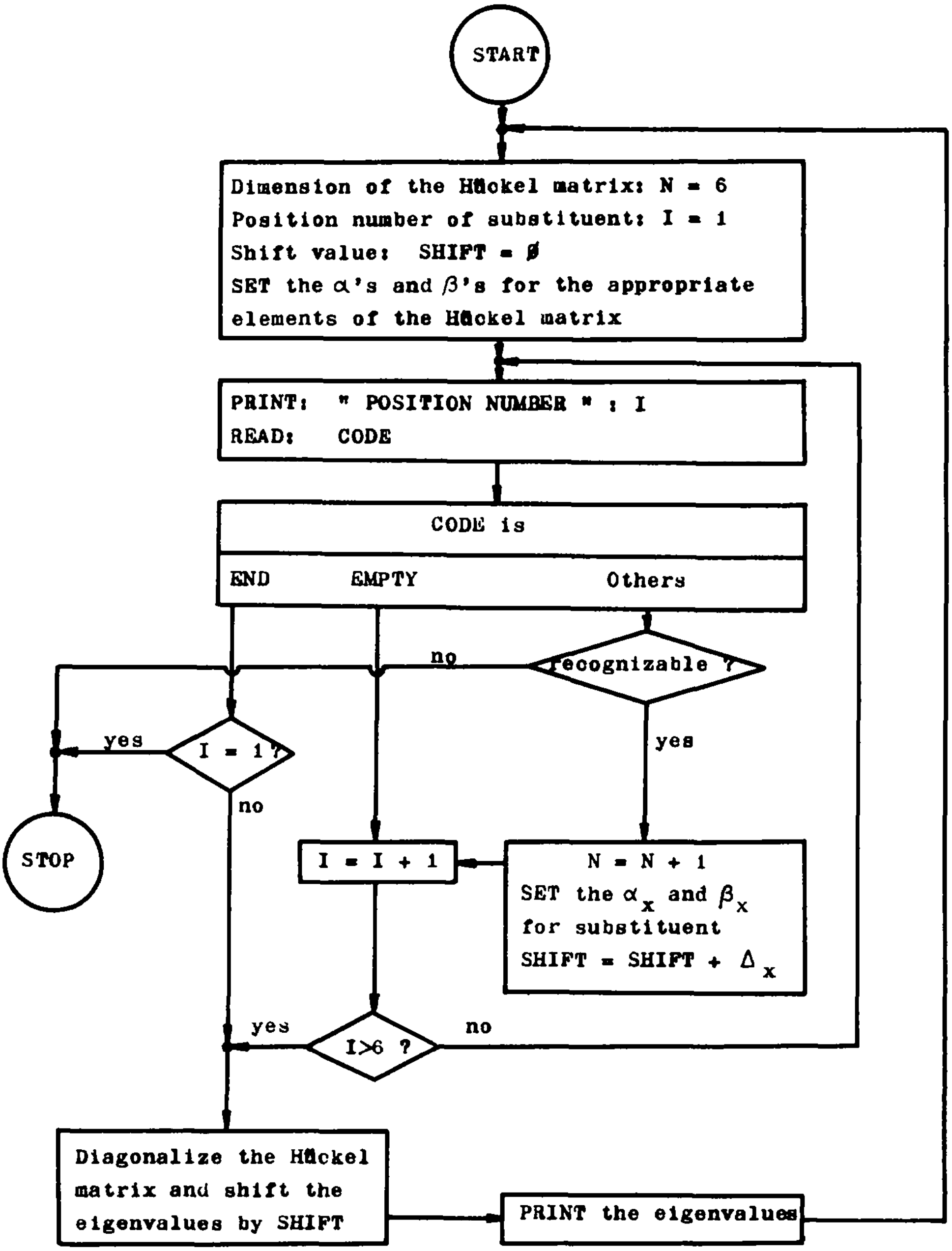


Fig.1. Simplified flowchard of the algorithm.

THEORY

In the Hückel method[15] the Hartree-Fock operator's matrix elements are approximated as follows:

$$F_{\mu\nu} = \begin{cases} \alpha_{\mu} & \text{when } \mu = \nu \\ \beta_{\mu\nu} & \text{when atoms } \mu \text{ and } \nu \text{ are bonded} \\ 0 & \text{in all other cases} \end{cases}$$

The α_{μ} and $\beta_{\mu\nu}$ parameters are fitted to yield theoretical results comparable with experimental data. In the case of the benzene molecule such a treatment, together with the application of Koopmans theorem[16], gives $\alpha_C = -6.20$ eV and $\beta_{CC} = -3.05$ eV, taking into account the experimental values of the first three IP's[17] (9.25 , 9.25 and 12.30 eV).

The influence of the substituent on the π-IP's is estaimated as follows:

1° Every substituent is treated as one pseudoatom supplying to the electron system two π electrons occupying one orbital. The pseudoatom is described by 2 parameters: α_X and β_{CX}. Thus, for instance trimethylbenzenes are assumed to consist effectively of 9 atoms having 6 occupied and 3 empty orbitals. For conjugated substituents, such as e.g. $-NO_2$, such a treatment although at the first sight dubious, was found to work quite well.

2° The inductive effect of the substituent is simulated by an addition of a constant term to all the calculated IP's. This term is the sum of the increments Δ_x for the substituents. A similar approach was used in the LCBO calculations.[9]

3° The parameters α_x, β_{ox} and Δ_x are computed assuming, that the first three π-IP's of the C_6H_5X molecule are to be exactly evaluated. Thus for every X the molecule C_6H_5X is used for fitting of α_x, β_{ox} and Δ_x. The parameters obtained in this way are presented in Table 1.

Table 1. The HMO parameters

X	Ref.	α_x [eV]	β_{ox} [eV]	Δ_x [eV]
CH_3	10	-13.60	-2.60	0.00
OCH_3	19	-12.30	-3.20	0.00
CN	14	-10.99	-1.66	0.87
C≡CH	14	-10.19	-1.93	0.23
NH_2	12	- 9.77	-2.70	-0.02
OH	11	-11.51	-2.65	0.03
NO_2	13	-10.56	0.00	0.67
F	18	-14.16	-2.71	0.38
Cl	20	-11.04	-2.07	0.39
Br	20	-10.37	-1.90	0.38

The α's, β's and Δ's thus determined are expected to give reasonable values for the π-IP's of polysubstituted benzenes, since they take in some terms due to electron correlation and relaxation effects. Nevertheless, it should be pointed out that these parameters seem to have no physical meaning and are at best empirical quantities giving results, in good agreement with experiments.

RESULTS AND DISCUSSION

The PE spectra of fluoro, methyl, hydroxy, nitro, cyano and amino substituted benzenes have been intensively studied by Palmer et al[10-14]. The experimental data of these authors were used to test the reliability of the algorithm presented. The data for ethynyl and methoxy substituents were taken from other papers.[21-23] The measured and calculated π-IP's are collected in Table 2 and Fig.2. The rms errors are 0.14 eV, 0.16 eV and 0.22 eV for the first, second and third π-IP's, respectively. It is to be noted, that this comparison refers also to ortho-disubstituted benzenes in which steric effects play an important role. The largest errors are encountered for o-dihydroxy- and o-diaminobenzene due to the possibility of the formation of hydrogen bonds in these compounds. In general, the method works quite weel for a broad spectrum of disubstituted benzenes.

Examples of application

A. Methylbenzenes. The approach described was used to estimate the first two IP's of toluene, o- and p-xylenes, mesitilene, durene and hexamethylbenzene. At the same time, the calculations invoking CNDO/S and MNDO were carried out for these compounds.[25] The estimated MO energies are collected in Table 3 together with the available[24] first two vertical ionization potentials. From an inspection of this table it is evident that the CNDO/S calculations using MNDO optimized geometry gives the best results when the calculated IP's are properly scaled (Table 3). The MNDO method gives completely unreliable results. The proposed algorithm yields IP's in quite good agreement with experiment. However, the required CPU time for a HMO calculation is about 10 000 times shorter than for CNDO/S one.

B. trans-β-Nitrostyrenes. The determination of the IP's of alkenes is important for predicting of their reactivity in cycloaddition reactions.[2] In order to check the performance and accuracy of the method, we have determined the first vertical ionization potentials of some trans-β-nitrostyrenes using standard PES measurements. The obtained data were used to determine the parameters of trans-$-CH=CHNO_2$ substituent by least square fitting. The parameters determined are: $\alpha = -9.40$ eV, $\beta = -0.31$ eV, $\Delta = 0.01$ eV. The CNDO/S and MNDO calculations were also performed. The results are given in Table 4. Again, the HMO method is comparable in accuracy to the CNDO/S. The MNDO method gives IP's overestimated by about 0.7 eV.

C. Benzonitrile N-oxides. Benzonitrile N-oxides serve as the last example. They form a class of compounds of great importance, since they constituti 1,3-dipoles in [2+3] cycloaddition reactions. The experimental values of their first three IP's were taken from the papers of Houk et al[26] and Bastide et al[27]. The parameters for $-C\equiv N\rightarrow O$ group determined by least square fitting are: $\alpha = -9.43$ eV, $\beta = -1.69$ eV, $\Delta = 0.55$ eV. As in the previous cases the HMO method presented here gives π-IP's close to the experimental values (Table 5).

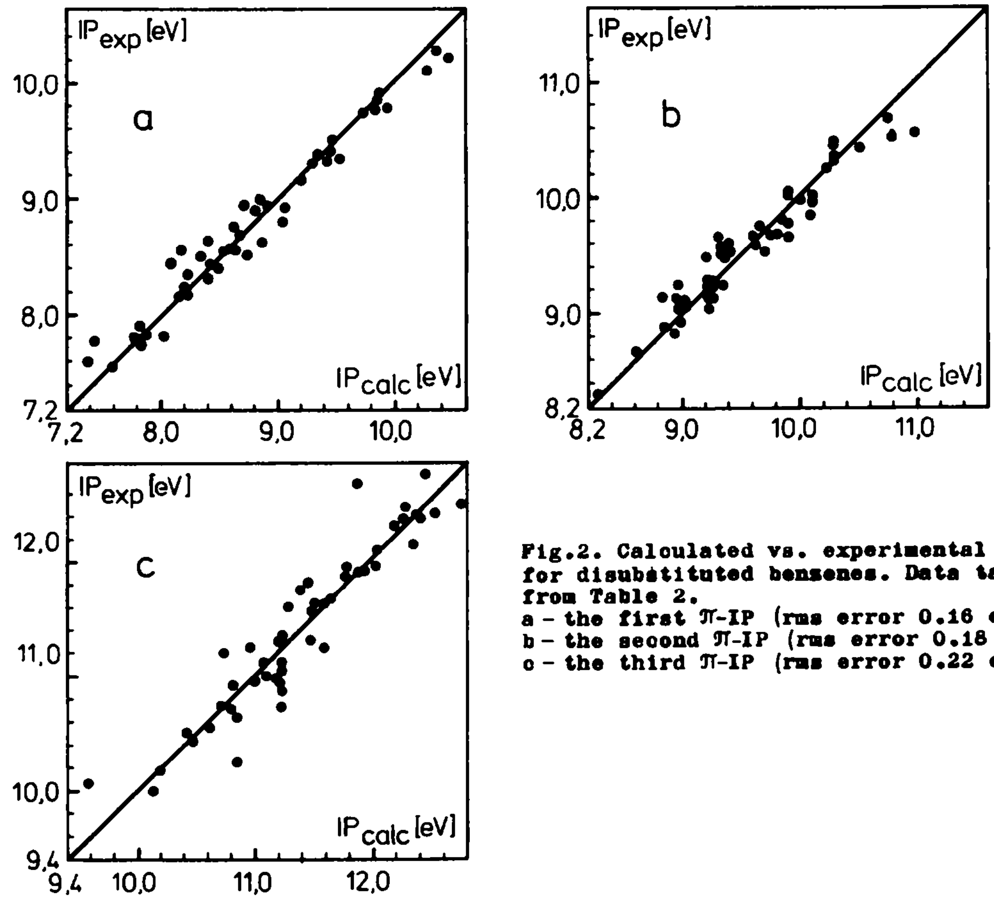


Fig.2. Calculated vs. experimental IP's for disubstituted benzenes. Data taken from Table 2.
a – the first π-IP (rms error 0.16 eV)
b – the second π-IP (rms error 0.18 eV)
c – the third π-IP (rms error 0.22 eV)

Table 2. The comparison of the calculated and experimental IP's for C_6H_4XY compounds

Substituents X/Y	/position/	Ref.	π- ionization potentials (exp/calc) [eV]		
CH_3/CH_3	/o/	10	8.56/8.53	9.07/9.04	11.67/11.65
CH_3/CH_3	/m/		8.56/8.64	9.05/8.99	11.62/11.52
CH_3/CH_3	/p/		8.44/8.42	9.15/9.25	11.80/11.46
NH_2/NH_2	/o/	12	7.78/7.44	8.67/8.62	10.74/10.72
NH_2/NH_2	/m/		7.74/7.84	8.31/8.30	10.18/10.20
NH_2/NH_2	/p/		7.61/7.39	9.48/9.21	10.07/ 9.58
NH_2/CH_3	/o/	12	7.84/7.86	8.84/8.94	10.63/10.83
NH_2/CH_3	/m/		7.82/8.02	8.89/8.87	10.55/10.62
NH_2/CH_3	/p/		7.81/7.80	9.06/9.23	10.50/10.42
CN/CN	/o/	14	10.27/10.36	10.52/10.79	12.50/12.80
CN/CN	/m/		10.20/10.45	10.68/10.75	12.42/12.55
CN/CN	/p/		10.10/10.27	10.56/10.99	12.38/12.41
CN/CH_3	/o/	14	9.40/9.45	9.79/9.91	11.96/12.03
CN/CH_3	/m/		9.34/9.54	9.81/9.87	11.90/11.89
CN/CH_3	/p/		9.38/9.35	10.01/10.12	11.93/11.79
OH/OH	/o/	11	8.56/8.17	9.25/8.97	11.60/11.29
OH/OH	/m/		8.63/8.40	9.15/8.85	11.25/10.96
OH/OH	/p/		8.44/8.08	9.66/9.31	11.21/10.74
OH/CH_3	/o/	11	8.50/8.33	9.12/9.03	11.76/11.40
OH/CH_3	/m/		8.41/8.48	9.14/8.96	11.31/11.20
OH/CH_3	/p/		8.35/8.24	9.24/9.28	11.12/11.08
C≡CH/C≡CH	/o/	21	8.69/8.67	9.25/9.36	10.98/11.19
C≡CH/C≡CH	/m/		8.62/8.85	9.39/9.24	10.72/10.80
C≡CH/C≡CH	/p/		8.58/8.59	9.54/9.71	10.43/10.47
F/F	/o/	10	9.30/9.30	9.68/9.81	12.75/12.46
F/F	/m/		9.32/9.42	9.68/9.76	12.14/12.35
F/F	/p/		9.15/9.20	9.98/10.01	12.46/12.30
CH_3/F	/o/	10	8.93/8.92	9.53/9.42	12.08/12.06
CH_3/F	/m/		8.80/9.03	9.48/9.38	11.91/11.94
CH_3/F	/p/		8.90/8.81	9.60/9.63	12.68/11.88
NH_2/F	/o/	12	8.18/8.24	9.58/9.33	10.95/11.21
NH_2/F	/m/		8.32/8.40	9.30/9.26	10.96/11.01
NH_2/F	/p/		8.18/8.18	9.67/9.61	10.91/10.82
CN/F	/o/	14	9.78/9.84	10.31/10.30	12.36/12.42
CN/F	/m/		9.79/9.93	10.26/10.25	12.36/12.28
CN/F	/p/		9.74/9.74	10.44/10.50	12.30/12.19
OH/F	/o/	11	8.95/8.71	9.60/9.41	11.86/11.79
OH/F	/m/		8.99/8.86	9.52/9.35	11.62/11.60
OH/F	/p/		8.77/8.62	9.75/9.66	11.57/11.49

Table 2 continued

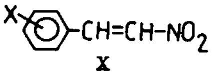
Substituents X/Y	/position/	Ref.	π- ionization potentials (exp/calc) [eV]		
NO_2/F	/o/	13	9.86/9.86	10.37/10.30	11.29/11.23
NO_2/F	/m/		9.88/9.86	10.47/10.30	11.35/11.23
NO_2/F	/p/		9.90/9.86	10.45/10.30	11.12/11.23
NO_2/CH_3	/o/	13	9.50/9.47	9.66/9.92	10.73/11.23
NO_2/CH_3	/m/		9.50/9.47	10.04/9.92	10.73/11.23
NO_2/CH_3	/p/		9.50/9.47	10.03/9.92	10.88/11.23
OCH_3/CN	/p/	22	8.92/9.06	9.97/10.12	11.24/11.59
NH_2/CN	/p/		8.51/8.73	9.85/10.10	11.00/11.09
OCH_3/NH_2	/p/	23	7.58/7.59	9.15/9.23	10.00/10.13
OCH_3/OCH_3	/p/		7.90/7.85	9.24/9.25	10.25/10.84
OCH_3/CH_3	/o/	19	8.24/8.21	8.94/8.99	11.31/11.48

Table 3. The comparison of the experimental and calculated π-IP's for methylbenzenes

Compound	π- ionization potential [eV]			
	Experimental 24	CNDO/S 1/ 25	MNDO 25	This work
toluene	8.78	8.69	9.28	8.80
	9.00	9.14	9.40	9.25
o-xylene	8.45	8.48	9.23	8.53
	8.90	8.87	9.33	9.04
p-xylene	8.37	8.31	9.18	8.42
	9.05	9.10	9.41	9.25
mesitylene	8.42	8.49	9.25	8.64
durene	8.10	8.01	9.10	8.04
	8.60	8.61	9.27	8.82
hexamethylbenzene	7.86	8.00	9.08	8.04

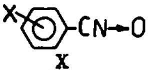
1/ Scaled by equation: $IP = 1.179\ IP_{calc} - 2.53$ [eV]

Table 4. The comparison of the experimental and theoretical IP's for trans-β-nitrostyrenes

	π- ionization potentials [eV]			
	Experimental	CNDO/S 1/	MNDO	This work
H	9.12	9.17	9.73	9.14
$p-CH_3$	8.79	8.86	9.64	8.77
$p-OCH_3$	8.50	8.88	9.27	8.43
p-CN	9.56	9.20	10.08	9.68
$p-NO_2$	9.83	-	10.56	9.79
p-F	9.25	9.18	9.81	9.16
p-Cl	9.04	-	9.91	9.05
m-Cl	9.22	-	10.00	9.07
p-Br	8.96	-	-	8.97

1/ Scaled by the equation: $IP = 1.179\ IP_{calc} - 2.53$ [eV]

Table 5. The comparison of the theoretical and experimental π-IP's for benzonitryle N-oxides

	π- ionization potentials [eV]		
	Experimental	Ref.	This work
H	8.96, 9.80, 10.84	27	8.96, 9.80, 10.84
2,6-diCH_3	8.62, 9.18, 10.55	27	8.71, 9.19, 10.83
2,4,6-triCH_3	8.35, 9.05, 10.26 8.34, 9.00, 10.24	27 26	8.51, 9.19, 10.53
4-OCH_3	8.42, 9.71, 10.16	26	8.50, 9.80, 10.34
2,4,6-triOCH_3	7.9, 8.7, 9.9	26	8.18, 8.79, 10.23
4-NO_2	>9.5	26	9.63, 10.47, 11.51

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