Electro-Optical Parameters of Some Benzene Derivatives obtained by Molecular Orbital Calculations

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A series of structural and physico – chemical properties of some monosubstituted halogene – derivatives of benzene were analyzed by using HyperChem software package. The bond lengths, the angle between the covalent bonds, atomic charges, the symmetry class, the energies of the ground and excited states, the dipole moments, the polarizabilities, the wavelengths of the electronic transitions and the corresponding oscillator strengths have been obtained and correlated with experimental data published for the studied compounds. The computed molecular polarizability α is directly correlated with the measured halogene atomic electronegativity. A polynomial dependence of order two was evidenced between the valence vibration wavenumber of C-X bond, experimentally determined and the computed polarizability.

Keywords: dipole moment, polarizability, energetic levels, electronegativity of halogen

HyperChem [1] - one of the most frequently used programmes in physics-chemistry- permits to build and to analyse various molecular structures (hydrocarbons, alcohols, acids, aminoacids, polymers) and to determine their physical and chemical properties.

The main steps to be followed in the general case are here described.

1. In order to build any type of molecule the following algorithm is used:

- the atoms' placement for the creation of a 2D-aspect of the molecule (for the organic molecules the placement begins with the C-atoms);
- the establishment of the bond type among the atoms;
- the addition of the hydrogen atoms for completing the valence;
- the realization of the 3D-aspect of the molecule by using the model build option.

2. The physical properties that can be determined are:

- the lengths of the bonds among various atoms;
- the angles between the bonds;
- some physical characteristics of the molecule; polarizability, dipole moment, electronic spectra [2] a.s.o.

3. Bonding and antibonding orbitals permit the achievement of the energetic level diagram. The electron distribution on the energetical levels and the allowed and forbidden transitions are also established.

4. From the analysis of the vibration electronic spectra can be determined: the degeneracy, the spin multiplicity, the oscillator strength, the vibration modes.

5. Graphical representation of the electrostatic potential.

6. Symmetry class: one molecule is characterized by its affiliation to a point group of symmetry. The symmetry operations of a given group (rotations, reflections) do not modify the molecular configuration.

7. Hartree-Fock method is an iterative procedure for solving the Schrödinger equation for an atom or molecule. The solution (the potential that results) is used to repeat the calculation, the procedure continuing until convergence is reached. This method is called self-consistent field (SCF) method, being used for determination of electronic structure.

Dipole moments are calculated with AM1, a semi-empirical SCF (Self – Consistent – Field) method for chemical calculations (electronic properties, optimized geometries, total energy, and heat for formation). This method is useful for organic molecules containing elements from long rows 1 and 2 of the periodic table, but not transition metals. Together with PM3 [3, 4], AM1 is generally the most accurate semi – empirical method included in HyperChem.

Results and discussions

In order to illustrate the statements from above, some halogeno-derivative molecules were chosen.

All considered halogen-derivatives of benzene belong to C_{2V} point group [5, 6], having as symmetry elements the molecular plane, $\sigma_V^{(1)}$, the plane perpendicular on the former and containing C-X bond, $\sigma_V^{(2)}$, and their crossing line as a C_2 axis.

All the corresponding symmetry operations, $\sigma_V^{(1)}$, $\sigma_V^{(2)}$, C_2 and the identity, E, do not change the spatial distribution of the molecular atoms.

In figure 1 the structure of the mono-halogen-benzene derivatives and the denomination of the molecular atoms are given.

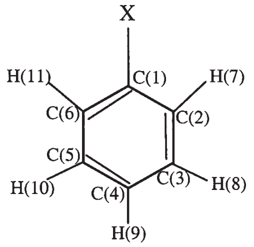

Fig. 1. Mono-substituted halogen - benzene derivative structure, X=F, Cl, Br, I

In figure 2 the electron distribution on the energetic levels is illustrated for the analysed mono-halogen-substituted benzene. On these graphs we can observe the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). The molecular orbitals computed by HyperChem have several important properties. Each molecular orbital has a uniquely defined orbital energy. Interpretation of orbital energies gives useful predictions. For example, the highest energy-occupied molecular orbital (HOMO)is important in

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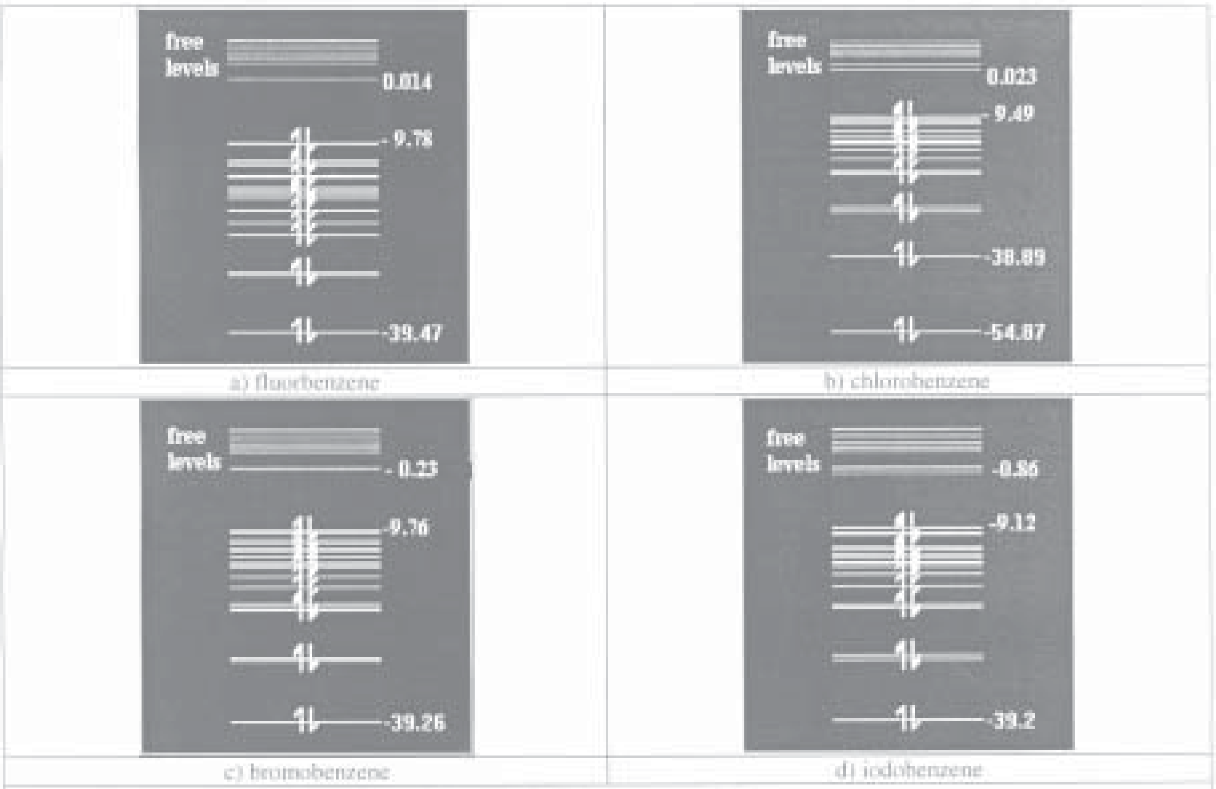

Fig. 2. Electron distribution on the energetic levels of the halogeno mono-substituted benzene derivatives

estimating the first ionization potential. Orbital energies are also important in interpreting molecular geometry and chemical reactivity.

Table 1
BOND LENGTH AND ANGLE BETWEEN BONDS

Substance	Bond length (Å)	Angle between bonds
Fluorobenzene	C-C:1,4 C-H: 1,08 C-F: 1,33	(C,C,C) =120^0 (Cl,C,C)=120^0 (H,C,C)=120^0
Chlorobenzene	C-C:1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C)=120^0 (Cl,C,C)=120^0 (H,C,C)=120^0
Bromobenzene	C-C:1,4 C-H: 1,08 C-B: 1,91	(C,C,C)=120^0 (Cl,C,C)=120^0 (H,C,C)=120^0
Iodobenzene	C-C:1,4 C-H: 1,08 C-I: 2,1	(C,C,C)=120^0 (Cl,C,C)=120^0 (H,C,C)=120^0

In table 1 the computed structural characteristics (length of interatomic bonds, angles between bonds) are given. From table 1 results that only C-X bond length varies in the mono-halogene-benzene derivatives class. The angles between the covalent bonds are 120^0, showing a sp^2 hybridization of all carbon atoms in the benzene cycles.

Table 2
POLARIZABILITY, DIPOLE MOMENT OF THE HALOGENO MONO-SUBSTITUTED BENZENES ESTIMATED BY HYPERCHEM AND THE EXERIMENTAL HALOGEN ELECTRONEGATIVITY χ (eV)

Substance	Polarizability (10^{-24} cm^3)	Dipole moment (D)	χ (eV)
Fluorobenzene	10.34	1.486	3,98
Chlorobenzene	12.36	1.519	3,16
Bromobenzene	13.06	1.503	2,96
Iodobenzene	15.46	1.515	2,66

Table 2 contains some physical parameters (polarizability and dipole moment) estimated by HyperChem and also the halogene electronegativites.

The polarizabilities were calculated with QSAR (Quantitative Structure-Activity Relationships) [7], a HyperChem module that allow us to compute a number of molecular physical parameters. These calculations generally sum atom contributions and are very fast.

In table 3 the atomic charges, estimated by HyperChem, are given.

Table 4 contains the computed wavelengths and oscillator strengths for the electronic transitions in the case of isolated molecules. They are located in the ultraviolet range. For comparison, in table 5 are listed the experimentally determined wavelengths and also logarithm from the extinction coefficients [8] in the case of halogeno-benzene derivative in ethanol solution.

Table 3
ATOMIC CHARGES COMPUTED BY HYPERCHEM

Atoms	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
C(1)	0.152	0.071	0.048	0.044
C(2)	-0.006	-0.012	-0.016	-0.017
C(3)	-0.028	-0.030	-0.030	-0.030
C(4)	-0.031	-0.031	-0.031	-0.031
C(5)	-0.028	-0.030	-0.030	-0.030
C(6)	-0.006	-0.012	-0.016	-0.017
H(7)	0.034	0.033	0.032	0.032
H(8)	0.131	0.031	0.031	0.031
H(9)	0.131	0.031	0.031	0.031
H(10)	0.131	0.031	0.031	0.031
H(11)	0.134	0.033	0.032	0.032
X	-0.239	-0.116	-0.083	-0.077

In order to check the validity of our results, the halogen substituent electronegativity has been taken into account. Electronegativity is a measure of the ability of an atom or molecule to attract electrons in the context of a chemical bond. Two scales of electronegativity are in common use: the Pauling scale (proposed in 1932) and the Mulliken scale (proposed in 1934).

The Pauling scale was introduced in 1932. On this scale, the most electronegative chemical element is fluorine and the least electronegative element is francium.

By considering that the energy used for changing the molecule from AB into the states A^+B^- and A^-B^+ is the same, if the atoms A and B have the same electronegativity, Mulliken [9] proposed a new scale, in which the electronegativity is expressed by:

$$\chi = \frac{1}{2}(I + A) \qquad (1)$$

Where I is the atomic ionisation potential and A is the affinity for the electrons of A or B.

Jaffe [10] discussed the fact that Mulliken's definition is a statically one and the electronegativity must reflect the dynamics of the charges. So, he proposed the electronegativity as a derivative of the atomic energy versus the net charge q, by relation:

$$\chi = \frac{\partial E}{\partial q} = (I - A)q + \frac{1}{2}(I + A) \qquad (2)$$

In the case of a neutral atom (q=0), (2) is reduced to the definition proposed by Mulliken in relation (1). The ion electronegativity χ(q) is expressed, according to (2) as follows.

$$\chi(q) = \chi(0) + q(I - A) \qquad (3)$$

It results that the ionic electronegativity depends on the net positive charge of the ions.

Table 4

WAVELENGTHS AND OSCILLATOR STRENGTH FOR ELECTRONIC ABSORPTION LINES ESTIMATED BY HYPERCHEM

Substance	Wavelength (nm)	Oscillator strenght
Fluorobenzene	315,25 284,30 203,06 202,95 202,75	0,002 0,006 1,024 1,103 0,001
Chlorobenzene	303,82 283,94 269,44 209,51 207,79	0,002 0,017 0,004 1,044 0,881
Bromobenzene	309,57 305,66 302,77 280,32 204,87 203,75	0,003 0,003 0,002 0,004 1,073 0,959
Iodobenzene	248,55 235,95	0,254 0,128

The data from tables 4 and 5 illustrate a good accordance between the theoretical estimations by HyperChem and experimental values of the wavelengths in the UV range.

In order to check the validity of the results obtained by HyperChem applied to the mono-halogen-benzene derivatives, the atomic electronegativity [9] of the halogen substitutes was used.

In the halogen-derivatives of benzene, the increasing of the atomic electronegativity of the substituents determines the decreasing of the deformation capacity of the electronic cloud. It results that the molecular polarizability must decrease by the atomic substituent electronegativity increasing. Relation (4) has been established between the computed by HyperChem molecular polarizability and the halogen electronegativity, experimentally determined. The dependence (4) is given in figure 3.

Table 5

WAVELENGTHS IN THE MAXIMA OF ELECTRONIC ABSORPTION BANDS AND logε OF HALOGEN BENZENE DERIVATIVES

Substance	Solvent	λ_{max}	logε
Fluorobenzene	Alcohol	204 254	3.8 3.0
Chlorobenzene	Alcohol	210 264	3.9 2.3
Bromobenzene	Alcohol	210 264	3.9 2.3
Iodobenzene	Alcohol	226 256	4.1 2.9

$$10^{24}\alpha(cm^{-3}) = 24{,}3(cm^{-3}) - 3{,}61\,\chi(eV) \qquad (4)$$

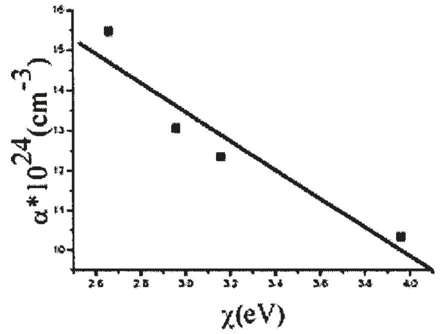

Fig. 3. Polarizability versus atomic electronegativity

A large value of the electronegativity corresponds to a high electron affinity of the substituient X, that contributes to a decrease in the force constant of C – X bond, and so to a decrease in the stretching vibrational wavenumber. The dependence between the wavenumber of C-X bond stretching vibration and the molecular polarizability estimated by HyperChem is illustrated in figure 4. The polynomial dependence between the wavenumbers of C-X stretching vibration experimentally determined and the computed molecular polarizability is given in relation (5).

$$\nu_{C-X}(cm^{-1}) = 1145{,}75 - 126{,}65 \cdot \alpha + 37{,}75 \cdot \alpha^2 \qquad (5)$$

The obtained dependences from figures 3 and 4 demonstrate the validity of the results obtained by HyperChem.

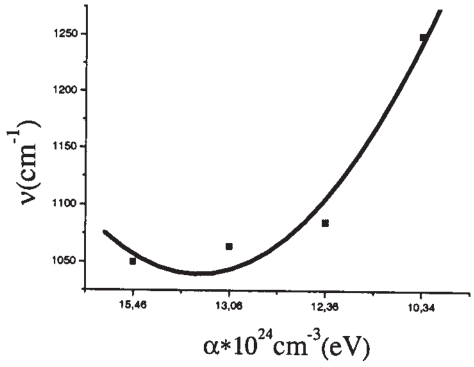

Fig. 4. $\nu_{c-x}(cm^{-1})$ versus molecular polarizability

Conclusions

The theoretical data obtained by HyperChem are in a good accordance with the experimental data published on the halogeno derivatives of benzene.

Even the results obtained by the computational methods refer to the isolated molecules and molecular spectroscopy offers information about the molecules included in the condensed state, a good qualitative accordance between theory and experiments has been observed.

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