

# ELECTRO-OPTICAL PARAMETERS OF SOME CHLOROBENZENE DERIVATIVES OBTAINED FROM THE MOLECULAR ORBITAL CALCULATION\*

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We analyzed a series of physicochemical properties and the geometry of some benzene chloride derivatives molecules using HyperChem. Physical and structural properties such as: bond length carbon - carbon and/or carbon-halogen, carbon-hydroxyl, the angle between different atoms of the bond, symmetry class, energies of the ground and excited states, dipole moment, polarizability have been obtained. From the electronic vibration spectra we establish the energy level diagram, level occupation numbers, oscillator strengths and the potential energy surface.

*Key words:* energy levels, dipole moment, polarizability, oscillator strength.

## INTRODUCTION

HyperChem – one of the most frequently used programmes in physics-chemistry – is used for building and analysing various molecular structures (hydrocarbons, alcohols, acids aminoacids, polymers) and for determining their physical and chemical properties.

### **The analysis of the molecular structures made by HyperChem programme**

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 of model build option.

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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 given molecule; polarizability, dipole moment.

3. Bonding and antibonding orbitals permit the achievement of the energetic levels' diagram, the electron distribution on the energetical levels, the allowed and forbidden transitions.

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

5. Graphical representation of the electrostatic potential.

6. Potential (energy) surface: A multidimensional plot of the potential energy of a molecular system, as a function of all of the variables (degrees of freedom), in the system (for example bond, angles). The potential surface for a molecule with  $N$  atoms has  $3N-6$  independent degrees of freedom (6 = three degrees reserved for rotation and three reserved for translation of the whole molecular system). Potential energy surfaces are usually diagrammed in only one or two dimensions. A 1D potential surface might show bond energy versus length. A 2D potential surface might show a contour plot of energy as a function of two torsion angles. Important features on a potential surface are minima, which HyperChem can locate with geometry optimization and molecular dynamics calculations, and saddle points, which represent structural transition states.

7. 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.

8. To describe the probability of a transition occurring a practical term is used which is commonly called the transition strength. To a first approximation, transition strengths are governed by selection rules which determine whether a transition is allowed or forbidden. Practical measurements of transitions strengths are usually described in terms of the Einstein A and B coefficients or the oscillator strength ( $f$ ). The oscillator strength of a transition is a dimensionless number that is useful for comparing different transitions. It is defined as the ratio of the strength an atomic or molecular transition to the theoretical transition strength of a single electron using a harmonic-oscillator model. Oscillator strengths can range from 0 to 1, or a small integer. A strong transition will have an  $f$  close to 1. Oscillator strengths greater than 1 result from the degeneracy of real electronic systems.

In order to illustrate the statements from above, the chloride benzene derivatives molecule were chosen.

## RESULTS AND DISCUSSION

1. The geometry of each studied molecule has been build using HyperChem (see Fig. 1)

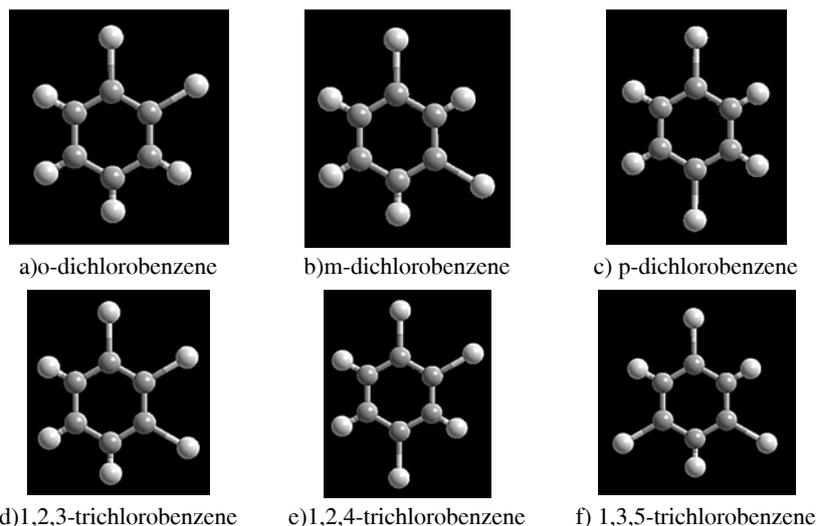


Fig. 1

In Table 1 the computed structural characteristics (length of interatomic bonds, angles between bonds) and physical properties (polarizability and dipole moment) estimated by HyperChem are given.

Table 1

Structural and physical characteristics of some chlorobenzene derivatives

Substance	Bond length [Å]	Angle between bonds	Polarizability [a.u]	Dipole moment (D)
chlorobenzen	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C) = 120° (Cl,C,C) = 120° (H,C,C) = 120°	56,016532	1,094
o-chlorobenzene	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C) = 120° (Cl,C,C) = 120° (H,C,C) = 120°	65,972657	1,608
m-chlorobenzene	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C) = 120° (Cl,C,C) = 120° (H,C,C) = 120°	67,217005	1,01
p-chlorobenzene	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C) = 120° (Cl,C,C) = 120° (H,C,C) = 120°	67,760580	5,218e-006

Table 1 (continued)

Substance	Bond length [Å]	Angle between bonds	Polarizability [a.u]	Dipole moment (D)
1,2,3-triclorbenzen	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C)=120° (Cl,C,C)=120° (H,C,C)=120°	76,642761	1,637
1,2,4-triclorbenzen	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C)=120° (Cl,C,C)=120° (H,C,C)=120°	78,396368	0,8109
1,3,5-triclorbenzen	C-C: 1,4 C-H: 1,08 C-Cl: 1,76	(C,C,C)=120° (Cl,C,C)=120° (H,C,C)=120°	79,146256	1,342e-005

From Table 2 it results that by passing from monochlorobenzene to di- or three chlorobenzenes the wavelength of the UV electronic lines increases with the number of the substituted chloro-atoms.

Table 2

Wavelengths and oscillator strength for electronic absorption lines estimated by HyperChem

Substance	Wavelength [nm]	Oscillator strenght	Symmetry class
chlorobenzene	207,79	0,881	$C_{2v}$
	209,51	1,044	
	269,44	0,004	
	283,94	0,017	
	303,82	0,002	
o-chlorobenzene	216,87	0,736	$C_{2v}$
	221,94	0,975	
	262,11	0,007	
	291,03	0,028	
	299,35	0,001	
m-chlorobenzene	215,62	0,729	$C_{2v}$
	221,80	0,985	
	233,13	0,003	
p-chlorobenzene	286,59	0,027	$D_{2h}$
	213,02	0,833	
	213,32	1,067	
	241,14	0,007	
	293,48	0,061	
	310,11	0,001	

Table 2 (continued)

Substance	Wavelength [nm]	Oscillator strenght	Symmetry class
1,2,3-thriclorobenzene	228,39	0,827	$C_{2v}$
	230,36	0,839	
	253,80	0,007	
	299,00	0,001	
	303,58	0,001	
1,2,4-thriclorobenzene	221,80	0,671	$C_s$
	226,57	0,001	
	228,61	0,995	
	246,20	0,002	
	297,77	0,065	
1,3,5-thriclorobenzene	225,76	0,878	$C_{2v}$

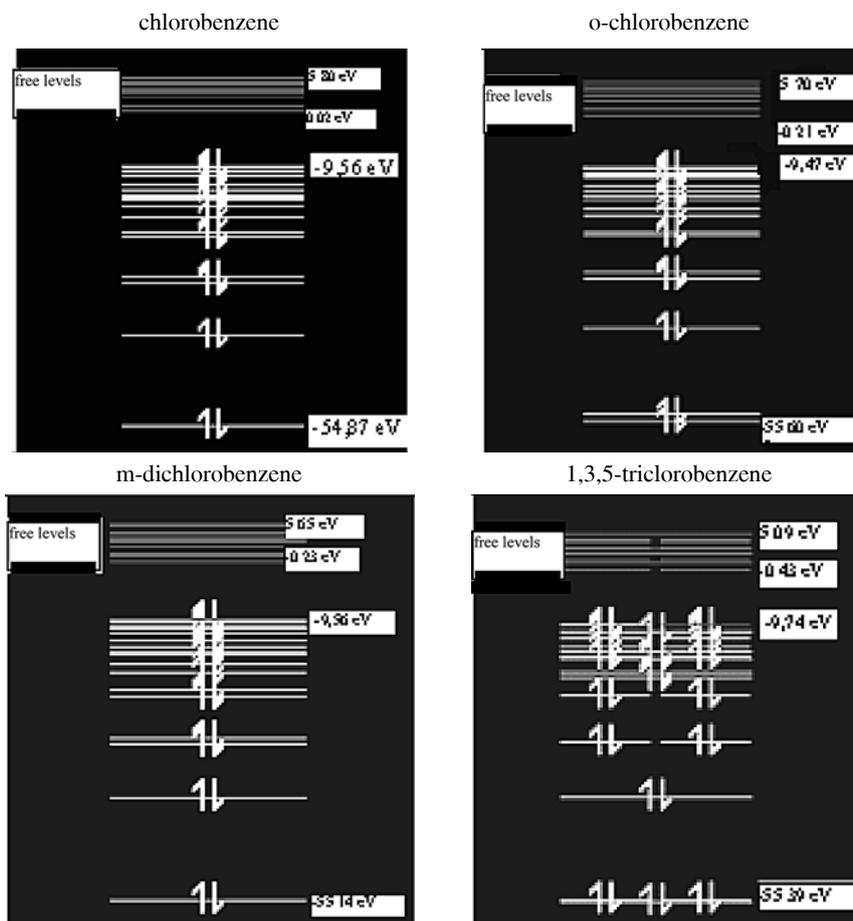


Fig. 2 – Computed electronic levels of some chloro-benzene derivatives.

From Fig. 2 it results the relative positions of the occupied and free energetic levels of the studied compounds.

The data from Tables 2 and 3 illustrate a good accordance between the theoretical estimations by HyperChem and experimental values of the wavelengths in the UV range.

Table 3

Wavelengths in the maxima of electronic absorption bands and  $\log \epsilon$  of chlorobenzene derivatives

Substance	Solvent	$\lambda_{\max}$	$\log \epsilon$	Ref
chlorobenzene	Alcohol	210	3.9	[1]
		264	2.3	
o-dichlorobenzene	Isooctane or trimethylpentan	219.5	3.6	[2]
		269	2.5	
m-dichlorobenzene	Alcohol	271	2.6	[3]
p-dichlorobenzene	Alcohol	225	4.1	[4]
		273	2.6	
1,2,3-trichlorobenzene	Cyclohexane	225.5		[2]
		272		
1,2,4-trichlorobenzene	Cyclohexane	226		[2]
		278		
1,3,5-trichlorobenzene	Alcohol	271	2.3	[5]

## CONCLUSION

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

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