

Nanomaterials for Photoelectrochemical Solar Cells: Computational Molecular Characterization of 3,4-Diphenyl-4-(4-Hydroxyphenyl)-1,2,5-Thiadiazoline 1,1-Dioxide

Norma Flores-Holguin¹, Luz Maria Rodriguez-Valdez² and Daniel Glossman-Mitnik^{*1}

¹Grupo NANOCOSMOS - Centro de Investigación en Materiales Avanzados, SC,
Complejo Industrial Chihuahua - Chihuahua, Chih. 31109 - Mexico

²Facultad de Ciencias Químicas - Universidad Autónoma de Chihuahua - Nuevo Campus Universitario - Chihuahua, Chih. 31125 - Mexico

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Abstract: In this work, we make use of a model chemistry within Density Functional Theory (DFT) recently presented, which is called CHIH-DFT, to calculate the molecular structure of 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{pheno}), as well to predict its infrared (IR), ultraviolet (UV-Vis) and fluorescence (Fluo) spectra, the dipole moment and polarizability, the free energy of solvation in different solvents as an indication of solubility, and the chemical reactivity parameters that arise from Conceptual DFT. The calculated values are compared with the available experimental data for this molecule as a means of validation of our proposed model chemistry.

Keywords: Molecular structure, IR, UV-Vis, Polarizability, Conceptual DFT

1. INTRODUCTION

Nanotechnology is an intersection - a confluence at the heart of contemporary science. It is where the latest breakthroughs in chemistry, physics and biology merge, mix with engineering and medicine, and produce chips, diagnoses and therapies that no sequestered specialist would generate. Nanotechnology produces convergent thinking when representative of various mind-sets meet, learn one another's languages, and gather the ideas that result when paradigms collide [1].

Most of the solar cells used in the terrestrial applications are bulk-type single- or multi-crystalline silicon solar cells. The typical cell structure is a thin (less than 1 μm) n-type emitter layer on a thick (about 300 μm) p-type substrate. Photo-generated electrons and holes diffuse to the space charge region at the interface where they are separated by the internal electric field. The effective charge separation results from long diffusion length of electrons and holes in crystalline silicon. Although it is aimed to reduce the solar cell module manufacturing cost, the drastic reduction of cell cost and increase of the conversion efficiency cannot be expected

by using the conventional materials and solar cell structures. Moreover, the shortage of the feedstock of high-purity silicon is predicted in the near future although it depends on off-spec silicon of electronics industry. Therefore, research and development of solar cells with low production cost, high conversion efficiency and low feedstock consumption are required [2].

An important concept to reach this goal is to use nanostructured materials instead of bulk materials. The motivations to employ nanostructures in solar cells are largely divided into three categories as follows: 1) To improve the performance of conventional solar cells; 2) To obtain relatively high conversion efficiency from low grade (inexpensive) materials with low production cost and low-energy consumption; 3) To obtain a conversion efficiency higher than the theoretical limit of conventional pn junction solar cell [2].

Organic solar cells are based on a heterojunction resulting from the contact of a donor (D) and an acceptor (A) material. Absorption of solar photons creates excitons, Coulombically bound electron-hole pairs, which diffuse to the D/A interface, where they are dissociated into free holes and electrons by the electric field. D/A heterojunctions can be created with two types of architectures, namely, bilayer heterojunction and bulk heterojunction (BHJ) solar

*To whom correspondence should be addressed:
Email: daniel.glossman@cimav.edu.mx

cells. BHJ cells combine the advantages of easier fabrication and higher conversion efficiency due to the considerably extended D/A interface. Recent years have seen the emergence of an alternative approach based on the re-placement of polydisperse polymers by soluble, conjugated single molecules as donor materials in BHJ cells. In fact, molecular donors present specific advantages in terms of structural definition, synthesis, and purification [3].

Quantum chemistry calculations can be helpful in predicting the behaviour of organic compounds, such as the physicochemical properties and the chemical reactivity, and thus they can be and aid in rationalizing the photovoltaic properties associated to this class of compounds.

The objective of this work is to perform a detailed calculation of the molecular structure of 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{phenol}), as well as to predict its infrared (IR), ultraviolet (UV-Vis), fluorescence (Fluo) spectra, some physical properties related to solubility and the chemical reactivity, by using a model chemistry within Density Functional Theory (DFT) [4] specially tailored to study heterocyclic systems [5] and to validate the calculated results by comparison with the available experimental data related to the molecular structure for this molecule. This compound has several desirable characteristics related to its use in Organic Photovoltaics and OLEDs: i) it contains the 1,2,5-thiadiazoline 1,1-dioxide group, with molecular parameters similar to the thiophene 1,1-dioxide derivatives that have been shown to be useful as nanostructured molecular materials; ii) the π -conjugated derivatives are generally efficient fluorophores, and as such, useful for the fabrication of nanobiosensors; iii) it can be used as an attractive building block for organic molecular materials that could be applied in photovoltaics.

2. THEORY AND COMPUTATIONAL DETAILS

All computational studies were performed with the Gaussian 03 series of programs [6] and the CHIH-DFT model chemistry, which uses our empirically modified functionals [5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. The implementation is a slightly different version of the PBE0 hybrid density functional [19]. Our proposed density functional model, which we have called *PBEg*, is the same as PBE0, but with the mixing coefficient g which adopts different values depending on the number of heteroatoms in the studied molecule, or, in turn, of its molecular structure, according to an empirical formula previously defined [5]. Thus, in our case for the 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{phenol}), the value of the mixing will be $g=0.50$, implying that 50% of Hartree-Fock (HF) exchange is mixed with 50% of DFT exchange. The correlation part is taken as the PBE correlation functional with coefficient equal to one [20].

In order to define our model chemistry, we have coupled the proposed density functional with several basis sets. In this way, the new model chemistry that we have called *CHIH DFT* can be represented by the expression $CHIH = PBEg/basis$ set. A detailed description of the model can be found in the original paper [5]. The *CHIH DFT* model chemistry has been already validated for the case of antiparasitic drugs [7, 8, 9], flavonoids [10, 11, 12], organic corrosion inhibitors [13, 14, 15], alkaloids [16, 17] and antitubercular drugs [18].

The equilibrium geometry of the studied molecule was determined by means of the gradient technique. The force constants and

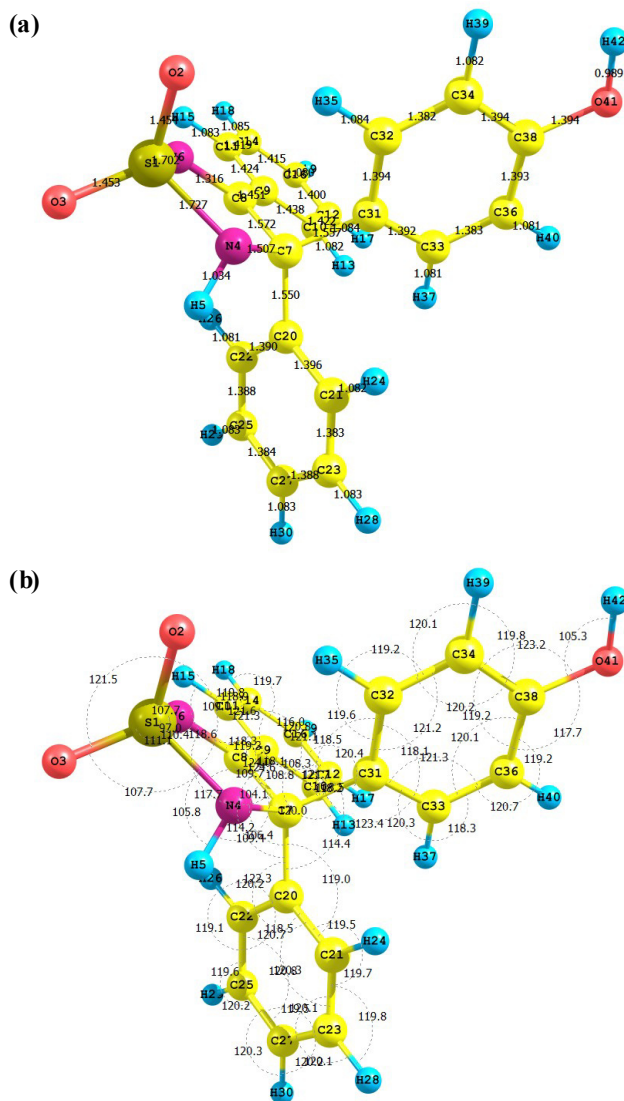


Figure 1. Interatomic bond distances (A) and bond angles (deg) for 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{phenol})

vibrational frequencies were determined from calculation using the FREQ keyword on the stationary points obtained after the optimization to check if there were true minima.

For the purpose of comparison, the molecular structure of the molecule has been computed using different model chemistries. Additional density functionals used in this study, are LSDA or SVWN [21, 22], BLYP [23, 24], B3LYP [25, 24], B3PW91 [25, 26], PBEPBE [20], PBE0 [19], TPSS [27] and TPSSH [28]. A suitable description of these density functionals is provided in some of the most important Computational Chemistry recent books [29, 30, 31, 32].

The calculation of the ultraviolet (UV-Vis) and fluorescence (Fluo) spectra of 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{phenol}) has been performed by solving

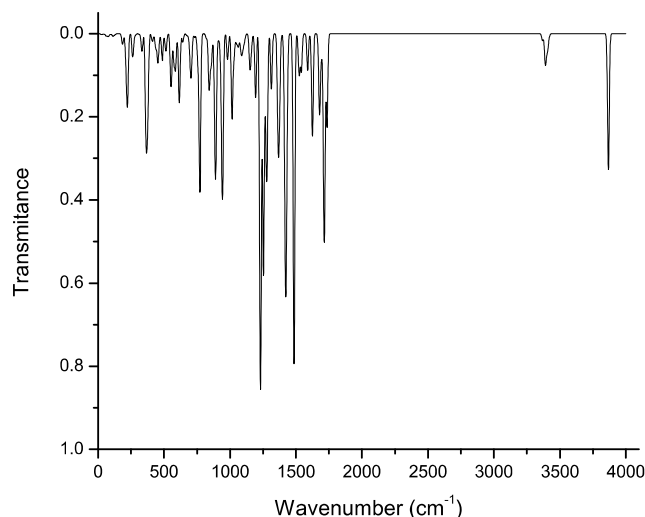


Figure 2. Infrared spectrum (IR) of the T_{phenol} molecule calculated with the *CHIH-DFT* model chemistry

the time dependent Kohn-Sham equations according to the method implemented in Gaussian03W [29, 33, 34, 35]. The equations have been solved for 10 excited states.

The infrared (IR), ultraviolet (UV-Vis) and fluorescence (Fluo) spectra were calculated and visualized using the Swizard program [36]. In all cases the displayed spectra show the calculated frequencies and absorption or emission wavelengths.

3. RESULTS AND DISCUSSION

The results for the equilibrium conformation of the neutral molecule of 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (or T_{phenol} , for short) calculated with the *CHIH(small)* model chemistry are presented in Figure 1 through a representation of the molecular structure showing the atomic labelling and numbering as well as the interatomic bond lengths and angles. The results have been compared with the experimental X-ray crystallography determination of the molecular structure of T_{phenol} [37]. The agreement is generally good: the standard error of the differences between the experimental and the calculated bond lengths and bond angles being very low. Although not shown in Figure 1, an analysis of the torsional angles reveals that the heterocycle is not planar, as expected, given the different hybridization of the N and C atoms. The good agreement with the experimental data is more noticeable for the heterocyclic ring, because the model have been parameterized for this kind of systems [5].

The infrared spectrum (IR) for the T_{phenol} molecule calculated with the *CHIH(small)* model chemistry is displayed in Figure 2. The experimental spectrum taken in KBr has been reported in the literature [37]. The vibrational band assignments have been done using the ChemCraft for Windows molecular visualization program. By comparison with the experimental IR spectrum, an average scaling factor of 0.97 could be estimated. Thus, it is expected that the model chemistry used in this work could reproduce the experimental spectrum of the T_{phenol} molecule with a certain degree of accuracy.

The ultraviolet spectrum (UV-Vis) of the T_{phenol} molecule calcu-

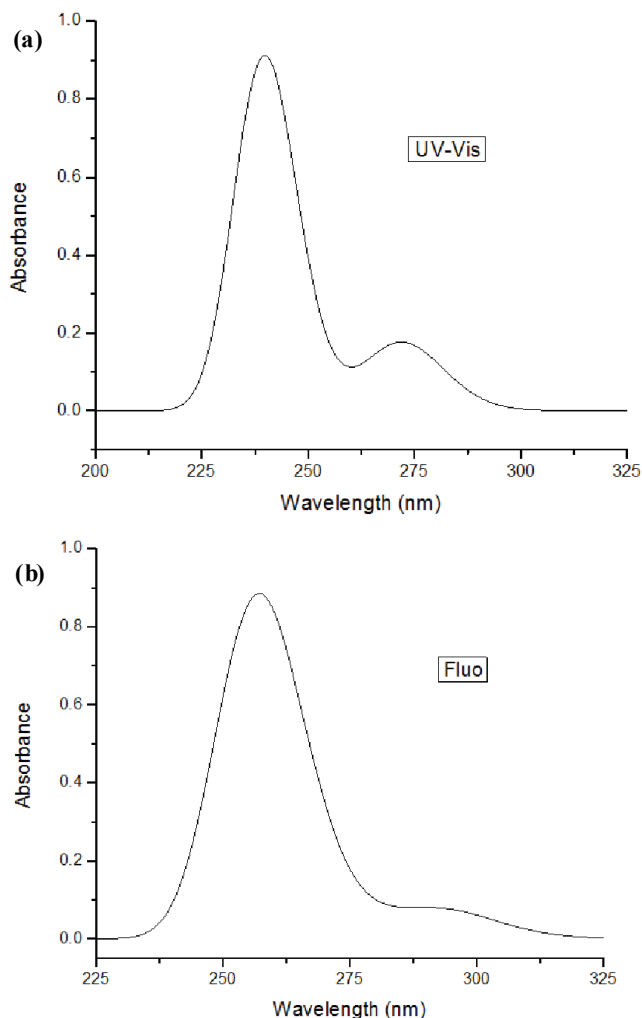


Figure 3. UV-Vis and fluorescence spectra of the T_{phenol} molecule calculated with the *CHIH-DFT* model chemistry

lated with the *CHIH(small)* model chemistry is displayed in Figure 3. The wavelength belonging to the HOMO-1-LUMO transition will take place at 235 nm, while the HOMO-LUMO transition will take place at 265 nm. As the HOMO-LUMO transition takes place in the ultraviolet region, close to but out of the visible zone, it can be predicted that this molecule will be colorless or slightly colored. In order to calculate the fluorescence spectrum of the studied molecule, the first excited state was optimized by using the CIS/3-21G(d) model chemistry. The results of a TDDFT calculation at the *CHIH(small)* model chemistry on the optimized excited state are also displayed in Figure 3, dubbed as the fluorescence (Fluo) spectrum. The wavelength belonging to the HOMO-1-LUMO transition now takes place at 257 nm, while the HOMO-LUMO transition takes place at 292 nm, although this last signal is very weak. This means that the studied molecule will not present fluorescence in the visible region.

The molecular dipole moment is perhaps the simplest experimental measure of charge distribution in a molecule. The accuracy of the overall distribution of electrons in a molecule is hard to quan-

tify, since it involves all the multipoles. The polarizability α contributes to the understanding of the response of the system when the external field is changed, while the number of electrons N is kept fixed. The polarizability is calculated as the average of the polarizability tensor $\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. From the present calculations, the total energy³, the total dipole moment and the isotropic polarizability of the ground state with the *CHIH(small)* model chemistry are -1503.771 au, 7.9407 Debye and 79.80 Bohr³ for the T_{phenol} molecule. These results could be of interest as an indication of the solubility and chemical re-activity of the studied molecule, not only for its synthesis but for the potential polymerization as a step in its use in organic electronics and photovoltaics.

The free energy of solvation $\Delta G(\text{solv})$ of the molecule have been calculated for T_{phenol} by resorting to the *CHIH(small)* model chemistry coupled with the Integral-Equation-Formalism of the Polarized Continuum Model (IEF-PCM) for different solvents as implemented in Gaussian 03.

The solubility of a molecule will depend on several kinetic and thermodynamic factors. However, it can be said that the magnitude and the sign of $\Delta G(\text{solv})$ could be a good approximation as an index of solubility. In this way, a negative sign and a large magnitude will be an indication of increased solubility. The results of these calculations for the studied molecule are presented in Table 1. These values could be an indication that the studied molecule will be mostly soluble in ethanol, methanol and acetone, and this can be related to the results obtained for the dipole moment and polarizability. However, the calculated results indicate that 3,4-diphenyl-4-(4-hydroxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{phenol}) will be more soluble in most solvents that its analogue 3,4-diphenyl-4-(4-methoxyphenyl)-1,2,5-thiadiazoline 1,1-dioxide (T_{anisol}).

The HOMO and LUMO of T_{phenol} calculated with the *CHIH(small)* model chemistry are displayed in Figure 4. The HOMO density corresponds to the heterocycle and the 4-hydroxyphenyl substituent, while the LUMO density is over the heterocyclic ring and the two phenyl rings. This can give us an idea of the reactivity of the molecule.

The reactive sites can be identified through an analysis of the total and orbital densities. The representation of the calculated HOMO and LUMO densities in Figure 4 show that the electrophilic

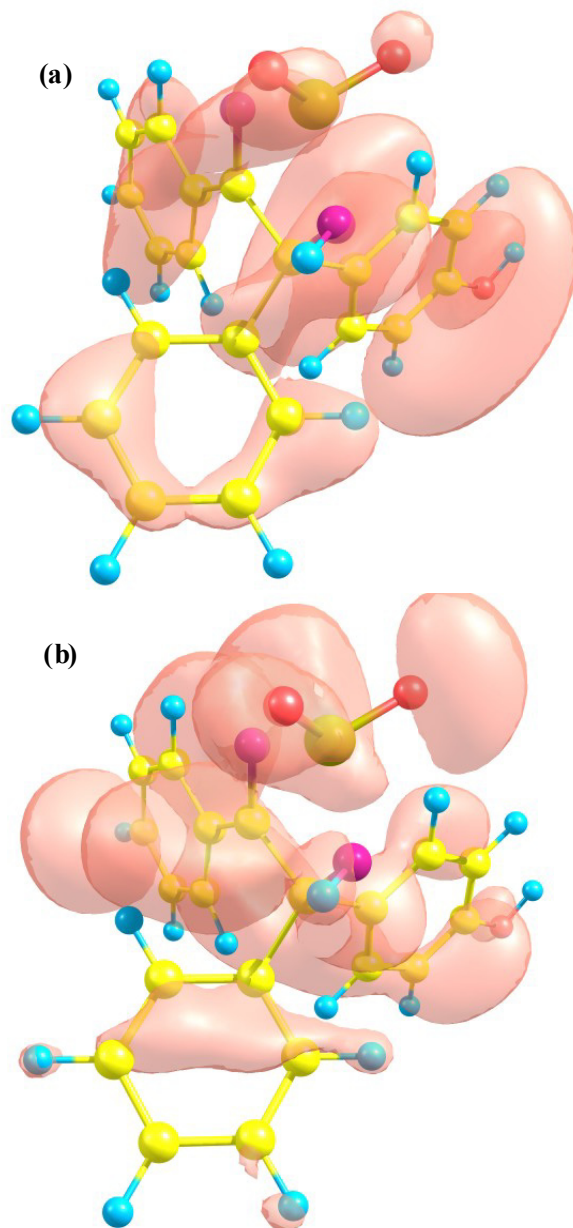


Figure 4. HOMO and LUMO of the T_{phenol} molecule calculated with the *CHIH-DFT* model chemistry

Table 1: Free energy of solvation (in Kcal/mol) for T_{phenol} calculated with the *CHIH(small)* model chemistry coupled with the Integral-Equation-Formalism of the Polarized Continuum Model (IEF-PCM) for different solvents

Solvent	$\Delta G(\text{solv})$	Solvent	$\Delta G(\text{solv})$
Acetone	-16.76	Diethylether	-6.64
Acetonitrile	-9.38	DMSO	-13.94
Aniline	3.46	Ethanol	-18.47
Benzene	-2.05	Heptane	-5.08
CCl4	-0.57	Methanol	-19.10
Chlorobenzene	-8.72	Nitromethane	-14.28
Chloroform	-8.72	THF	-9.89
Cyclohexane	-3.81	Toluene	-3.71
Dichloroethane	-12.42	Water	-12.21
Dichloromethane	-13.90		

attack would occur preferentially at the nitrogens and the nucleophilic attack at the heterocyclic ring carbons.

Within the conceptual framework of DFT [4], the chemical potential μ , which measures the escaping tendency of electron from equilibrium is defined as:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi \quad (1)$$

where χ is the electronegativity.

The global hardness η can be seen as the resistance to charge transfer:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v,r} \quad (2)$$

Using a finite difference approximation and Koopmans' theorem [29, 30, 31, 32], the above expressions can be written as:

$$\mu = \frac{I + A}{2} = \frac{H + L}{2} \quad (3)$$

$$\eta = \frac{I - A}{2} = \frac{H - L}{2} \quad (4)$$

where H and L are the energies of the highest occupied and the lowest unoccupied molecular orbitals, HOMO and LUMO, respectively.

The electrophilicity index ω represents the stabilization energy of the systems when it gets saturated by electrons coming from the surrounding:

$$\omega = \frac{\mu^2}{2\eta} = \frac{(I + A)^2}{2(I - A)} = \frac{(H + L)^2}{2(H - L)} \quad (5)$$

The validity of the Koopmans' theorem within the DFT approximation is controversial. However, it has been shown [38] that although the KS orbitals may differ in shape and energy from the HF orbitals, the combination of them produces Conceptual DFT reactivity descriptors that correlate quite well with the reactivity descriptors obtained through Hartree-Fock calculations. Thus, it is worth to calculate the electronegativity, global hardness and global electrophilicity for the T_{phenol} molecule using both approximations in order to verify the quality of the procedures.

The results for the vertical IP and A of the T_{phenol} molecule obtained through energy differences between the ionized and the neutral state, calculated at the geometry of the neutral molecule are IP = 8.285 eV and A = 1.066 eV. The HOMO and LUMO energies are -7.623 eV and 1.549 eV, respectively. It can be seen that there is a good qualitative agreement between both results. The calculated values of the electronegativity, global hardness and global electrophilicity using the IP and A are $\chi = 4.676$ eV, $\eta = 3.610$ eV and $\omega = 3.028$ eV. Using the HOMO and LUMO energies, within the Koopmans' theorem, the corresponding values are $\chi = 4.586$ eV, $\eta = 3.037$ eV, and $\omega = 3.463$ eV. Again, there is a good qualitative agreement for the reactivity parameters calculated through both procedures. It can be concluded that for the particular case of the T_{phenol} molecule, the CHIH-DFT model chemistry is able to predict the Conceptual DFT reactivity indices calculated through HOMO and LUMO energies as well as from the IP and A obtained through energy differences with qualitative similar good accuracy.

The condensed Fukui functions can also be employed to determine the re-activity of each atom in the molecule. The corresponding condensed functions are given by $f_k^+ = q_k(N+1) - q_k(N)$ (for nucleophilic attack), $f_k^- = q_k(N) - q_k(N-1)$ (for electrophilic attack), and $f_k^0 = [q_k(N+1) + q_k(N-1)]/2$ (for radical attack), where q_k is the gross charge of atom k in the molecule.

It is possible to evaluate the condensed Fukui functions from single-points calculations directly, without resorting to additional calculations involving the systems with N-1 and N+1 electrons,:

$$f_k^+ = \sum_{a \in k} \left[c_{ai}^2 + c_{ai} \sum_{b \neq a} c_{bi} S_{ab} \right] \quad (\text{where } i = \text{LUMO})$$

$$f_k^- = \sum_{a \in k} \left[c_{ai}^2 + c_{ai} \sum_{b \neq a} c_{bi} S_{ab} \right] \quad (\text{where } i = \text{HOMO})$$

with c_{ai} being the LCAO coefficients and S_{ab} the overlap matrix. The condensed Fukui functions are normalized, thus $\sum_k f_k = 1$ and $f_k^0 = (f_k^+ + f_k^-)/2$. The results from the calculation of the condensed Fukui functions for nucleophilic, electrophilic and radical attack have been obtained by resorting to the AOMix molecular analysis program [39] and are presented in Table 2.

The sites for electrophilic attack will be those atoms bearing a negative charge and where the Fukui function f_k^- is a maximum. These values confirm that the sites for the electrophilic attack is the N6 atom. The site for potential nucleophilic attack would depend on the values of f_k^+ on the atoms with a positive charge density. The results from Table 2 show that the site for nucleophilic attack will be the C31 atom. Finally, the sites for radical attack, governed by the values of f_k^0 will be the C8 and C31 atoms. The benzenic rings are not very reactive in this context.

4. CONCLUSIONS

In this work, our model chemistry within DFT (the CHIH-DFT chemistry model) has been presented and the methodology has been applied to the study of a molecule which is potentially useful for molecular photovoltaics. The molecular structure for the T_{phenol} molecule has been determined by using the CHIH(*small*) model chemistry. A comparison has been made with the results from the experimental X-ray crystallography for this molecule. The agreement is generally very good. It is worth noting that the results obtained with the (faster) CHIH(*small*) model chemistry are very similar to those obtained using the PBE0 functional with a CBSB7 basis set, thus implying that equally accurate results could be obtained in a reasonable time in the study of heterocycles. A general comparison with the results from the optimization of the molecular structure using several different density functionals have also been performed and the conclusion is that the CHIH-DFT is a good alternative to other model chemistries based on hybrids GGA and meta-GGA functionals for the prediction of molecular structures.

The shape of the frontier orbitals of this molecule were displayed as well as some electronic parameters like the total energy, the dipole moment and the polarizability. Moreover, the calculation of the condensed Fukui functions can be useful to obtain an idea of the chemical reactivity of the studied molecule. This is of special importance if we consider that the studied molecule could be the starting point for a polymeric material of potential application in organic electronics and photovoltaics, and that the chemical reactivity indices could assist the experimentalists in planning and guiding the synthetic and polymerization processes.

The infrared (IR) and ultraviolet (UV-Vis) and fluorescence (Fluo) spectra for T_{phenol} molecule have been predicted according to the CHIH(*small*) model chemistry, and an assignment of the principal peaks have been achieved. The shape of the UV-Vis spectrum and the maximum absorption wavelength belonging to this mole-

cule have been presented and this have been compared with the fluorescence spectrum. The results showed that the studied molecule could be an useful starting point for the preparation of materials of use in organic electronic and photovoltaics.

The free energy of solvation $\Delta G(\text{solv})$ of the molecule have been

Table 2. Condensed Fukui functions (X 100) calculated by using the *CHIH(small)* model chemistry and through the AOMIX molecular analysis program

Atom	Charge	f_k^+	f_k^-	f_k^0
1S	1.33	0.19	2.09	0.96
2O	-0.52	0.04	1.02	0.52
3O	-0.50	0.31	0.57	0.43
4N	-0.58	1.38	0.09	0.72
5H	0.29	0.12	0.01	0.07
6N	-0.53	1.23	19.26	9.96
7C	-0.10	0.63	0.38	0.50
8C	0.19	0.92	26.23	13.05
9C	0.03	0.52	7.40	3.39
10C	-0.10	0.69	10.52	5.13
11C	-0.10	0.07	10.09	6.14
12C	-0.14	0.18	1.29	0.66
13H	0.12	0.04	0.10	0.07
14C	-0.14	0.62	1.39	0.66
15H	0.18	0.01	0.09	0.07
16C	-0.11	0.32	14.33	8.45
17H	0.14	0.00	0.01	0.01
18H	0.14	0.01	0.01	0.01
19H	0.15	0.00	0.15	0.08
20C	-0.01	0.23	0.75	0.47
21C	-0.11	0.32	0.09	0.18
22C	-0.12	0.03	0.47	0.23
23C	-0.13	0.12	0.06	0.08
24H	0.15	0.06	0.01	0.03
25C	-0.13	0.22	0.03	0.12
26H	0.14	0.00	0.16	0.06
27C	-0.12	0.05	0.02	0.03
28H	0.14	0.01	0.02	0.02
29H	0.14	0.00	0.01	0.01
30H	0.14	0.00	0.01	0.01
31C	0.10	26.42	0.77	13.01
32C	-0.11	6.38	0.25	3.96
33C	-0.14	3.45	1.01	1.40
34C	-0.17	8.43	0.27	3.70
35H	0.18	0.03	0.03	0.04
36C	-0.13	13.50	0.25	7.58
37H	0.13	0.02	0.03	0.02
38C	0.23	19.06	0.58	9.10
39H	0.13	0.05	0.00	0.03
40H	0.14	0.08	0.01	0.05
41O	-0.48	14.10	0.10	7.97
42H	0.28	0.17	0.00	0.16

calculated for T_{phenol} molecule by resorting to the *CHIH(small)* model chemistry coupled with the Integral-Equation-Formalism of the Polarized Continuum Model (IEF-PCM) for different solvents and the results gave an indication of ethanol as the solvent in which this molecule could be potentially soluble.

The ionization potential IP and the electron affinity A have been calculated through energy differences between the ionic and the neutral states, all at the geometry of the neutral molecule, and they have been compared well with the results obtained from the HOMO and LUMO energies obtained through the Koopmans' theorem procedure. Several reactivity indices derived from Conceptual DFT like the electronegativity χ , the global hardness η , and the global electrophilicity ω have been obtained using the IP and A values, as well as the HOMO and LUMO energies, and the results indicate a qualitative good agreement, which can be considered an indication of the goodness of the proposed model chemistry.

The CHIH-DFT model chemistry appears to be a useful tool for the study of the molecular structure and electronic properties of heterocycles and the nanostructures derived from them, and further applications to several molecular systems are being pursued in our laboratory.

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