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Electronic Structure and Properties of 2Hydroxyanthracene in Gas Phase and in Ethanol: RHF and DFT Study

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Abstract

In this article, the molecular dynamics of the organic semi-conductor material 2-hydroxyanthracene in gas phase and in ethanol is examined using ab initio Quantum Chemical calculations at the Restricted-HartreeFock (RHF) level of theory by employing 6-31G basis set and Density Functional Theory (DFT) using the same basis set for inclusion of electron correlation. The molecular structure, dipole moment, quadrupole moment, charge transfer, polarizability, energy and vibrational frequencies with Infrared (IR) and Raman intensities have been studied. The change in polarizability tensors is found to be more pronounced in solution than in the gas phase.

Keywords: Electronic structure, organic semi-conductor, gas phase, ethanol.

1.0 Introduction

Electronic devices have continuously decreased in size during the last century, starting with meter-sized vacuum valve tubes of the early 1930’s and 1940’s, through millimeter-sized transistors in the 1960’s to micrometer-sized integrated circuits (microelectronics) in the 1970’s and 80’s. The microelectronics has also undergone relentless miniaturization during the past 25 years, leading to dramatic improvements in computational capacity and speed. But the end of that road is fast approaching, and scientists and engineers have been investigating another promising avenue: using individual molecules as functional electronic devices. Their nanometer–size and their ability to generate an electrical response to light may help the way to the development of molecular scale (Opto) electronic devices for communications, data processing and sensor applications [1].

Remarkable progress has been achieved both in new anthracene derivative synthesis and application in OFET. Methods for obtaining polymers with various content and position of anthracene groups in macromolecules (in the main chain, in the side radicals, or at the chain end) have been worked out. The methods are based on the copolymerization and on the reaction of synthetic and natural polymers with the participation of anthracene-containing monomers or reagents. The pecularities of the anthracene group reactivity in these reactions were investigated. Investigation of free radical copolymerization of 9-vinyl-anthracenes has shown that the reaction center can shift from the α-carbon of 9-anthrylmethyl system to the 10th position. This permits the preparation of polymers with anthracene groups in the main chains. The structure and content of the anthracene groups in the polymers obtained has been established (polyacrylic and polymethacrylic acids and their esters, polystyrene, polymethylene, polyvinylic ethers, some biopolymers) by UV-spectroscopy and by measurements of their luminescent parameters (spectra, lifetime of excitation, and polarization of fluorescence). The polymers with very low amount of anthracene groups “luminescent marks” (one per more than thousand of monomeric units), differently placed in macromolecules, have been used for investigating intramolecular motion of macromolecules by the method of polarized luminescence [2].This article provides a computational study of the electronic properties of the organic semiconductor material 2 Hydroxyanthracene. It highlights some of the molecular dynamic properties that are essential for the development of future opto-electronic devices [3]. Organic semi-conductors have many advantages, such as, easy fabrication, mechanical flexibility and low cost.

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2.0 Methodology

2.1 Theoretical Background of the Computational Method

The Schrodinger equation for a collection of particles like a molecule is very similar to that of a particle. In this case, Ψ, the wave function would be a function of the coordinates of all the particles in the system as well as the time, t [4].The energy and many other properties of the particle can be obtained by solving the Schrodinger equation for Ψ, subject to the appropriate boundary conditions. Many different wave functions are solutions to it, corresponding to different stationary states of the system.

For a molecular system, Ψ is a function of the positions of the electrons and the nuclei within the molecule, which we will designate as $\vec{r}$ and $\vec{R}$, respectively. These symbols are a shorthand for the set of component vectors describing the position of each particle. Note that electrons are treated individually, while each nucleus is treated as an aggregate; the component nucleons are not treated individually.

The kinetic energy is a summation of ∇^2 over all the particles in the molecule:

$$\mathrm{T}=-\frac{h^2}{8\pi^2}\sum_k\frac{1}{m_k}\left(\frac{\partial^2}{\partial x_k{}^2}+\frac{\partial^2}{\partial y_k{}^2}+\frac{\partial^2}{\partial z_k{}^2}\right) \tag{2.1}$$

The potential energy component is the Coulomb repulsion between each pair of charged entities (treating each atomic nucleus as a single charged mass):

$$\mathrm{V}=\frac{1}{4\pi\varepsilon_0}\sum_j\sum_{k<j}\frac{e_je_k}{\Delta r_{jk}} \tag{2.2}$$

Where Δr_{jk} is the distance between the two particles, and e_j and e_k are the charges on particles *j* and *k*. For an electron the charge is *–e*, while for a nucleus, the charge is *Ze*, where *Z* is the atomic number for that atom. Thus,

$$\mathrm{V}=\frac{1}{4\pi\varepsilon_0}\left\{-\sum_i\sum_I\frac{Z_Ie^2}{\Delta r_{iI}}+\sum_i\sum_{j<i}\frac{e^2}{\Delta r_{ij}}+\sum_I\sum_{J<I}\frac{Z_IZ_Je^2}{\Delta R_{IJ}}\right\} \tag{2.3}$$

The first term corresponds to electron-nuclear attraction, the second to electron-electron repulsion and the third to nuclear-nuclear repulsion [5].

The Born-Oppenheimer approximation is the first of several approximations used to simplify the solution of the Schrodinger equation. It simplifies the general molecular problem by separating nuclear and electronic motions. This approximation is reasonable since the mass of a typical nucleus is thousands of times greater than that of an electron. The full Hamiltonian for the molecular system can then be written as:

$$\mathrm{H}=\mathrm{T}^{elec}\left(\vec{r}\right)+\mathrm{T}^{nucl}\left(\vec{R}\right)+\mathrm{V}^{nucl-elec}\left(\vec{R},\vec{r}\right)+\mathrm{V}^{elec}\left(\vec{r}\right)+\mathrm{V}^{nucl}\left(\vec{R}\right) \tag{2.4}$$

The Born-Oppenheimer approximation allows the two parts of the problem to be solved independently, so we can construct an electron Hamiltonian which neglects the kinetic energy term for the nuclei. This Hamiltonian is then used in the Schrodinger equation describing the motion of electrons in the field of fixed nuclei.

ψ^2 isinterpreted as the probability density for the particle(s) it describes. Therefore, we require that ψ be normalized; if we integrate over all space, the probability should be the number of particles. Accordingly, we multiply ψ by a constant such that:

$$\int_{-\infty}^{+\infty}\left|c\psi\right|^2dv=n_{particles} \tag{2.5}$$

We can do this because the Schrodinger equation is an eigenvalue equation, and in general, if *f* is a solution to an eigenvalue equation, then *cf* is also, for any value of *c* [6].

The first approximation to be considered comes from the interpretation of $\left|\psi\right|^2$ as a probability density for the electrons within the system. Molecular orbital theory decomposes ψ into a combination of molecular orbitals: ϕ_1, ϕ_2, …. To fulfill some of the conditions on ψ, a normalised, orthogonal set of molecular orbitals is chosen as:

$$\iiint\phi_i^*\phi_i dxdydz=1$$

$$\iiint \phi_i^* \phi_j dxdydz = 0 \qquad i \neq j \tag{2.6}$$

The simplest possible way of making ψ as a combination of these molecular orbitals is by forming their Hartree product [7]:

$$\psi\left(\vec{r}\right) = \phi_1\left(\vec{r}_1\right)\phi_2\left(\vec{r}_2\right)...\phi_n\left(\vec{r}_n\right) \tag{2.7}$$

The simplest anti-symmetric function that is a combination of molecular orbitals is a determinant. However, most calculations are closed shell calculations, using doubly occupied orbitals, holding two electrons of opposite spin. For the moment, we will limit our discussion to this case.

We define two spin functions, α and β as follows:

$$\begin{aligned} &\alpha(\uparrow) = 1 \qquad \alpha(\downarrow) = 0 \\ &\beta(\uparrow) = 0 \qquad \beta(\downarrow) = 1 \end{aligned} \tag{2.8}$$

The α function is 1 for a spin up electron and the β function is 1 when the electron is spin down. The notation $\alpha(i)$ and $\beta(i)$ will designate the values of α and β for electron i; thus $\alpha(1)$ is the value of α for electron 1. We can now build a closed shell wave function by defining $n/2$ molecular orbitals for a system with n electrons and then assigning electrons to these orbitals in pairs of opposite spin.

$$\psi(\vec{r}) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}_1)\alpha(1) & \phi_1(\vec{r}_1)\beta(1) & \phi_2(\vec{r}_1)\alpha(1) & \phi_2(\vec{r}_1)\beta(1)...\phi_{n/2}(\vec{r}_1)\alpha(1) & \phi_{n/2}(\vec{r}_1)\beta(1) \\ \phi_1(\vec{r}_2)\alpha(2) & \phi_1(\vec{r}_2)\beta(2) & \phi_2(\vec{r}_2)\alpha(2) & \phi_2(\vec{r}_2)\beta(2)...\phi_{n/2}(\vec{r}_2)\alpha(2) & \phi_{n/2}(\vec{r}_2)\beta(2) \\ . \\ . \\ . \\ \phi_1(\vec{r}_n)\alpha(n) & \phi_1(\vec{r}_n)\beta(n) & \phi_2(\vec{r}_n)\alpha(n) & \phi_2(\vec{r}_n)\beta(n)...\phi_{n/2}(\vec{r}_n)\alpha(n) & \phi_{n/2}(\vec{r}_n)\beta(n) \end{vmatrix} \tag{2.9}$$

Each row is formed by representing all possible assignments of electron i to all orbital-spin combinations. The initial factor is necessary for normalization. Swapping two electrons corresponds to interchanging two rows of the determinant, which will have the effect of changing its sign.

The next approximation involves expressing the molecular orbitals as linear combinations of a pre-defined set of one-electron functions known as basis functions. These functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals. However, the actual mathematical treatment is more general than this and any set of appropriately defined functions may be used [9]. An individual molecular orbital is defined as:

$$\phi_i = \sum_{\mu=1}^{N} c_{\mu i}\chi_\mu \tag{2.10}$$

Where the coefficients $c_{\mu i}$ are known as the molecular orbital expansion coefficients. The basis functions $\chi_1....\chi_N$ are also chosen to be normalised. Gaussian and other ab initio electronic structure programs use gaussian-type atomic functions as basis functions. Gaussian functions have the general form:

$$g(\alpha,\vec{r}) = cx^n y^m z^l e^{-\alpha r^2} \tag{2.11}$$

Where $\vec{r}$ is composed of *x, y* and *z*. α is a constant determining the size (radial extent) of the function. In a gaussian function, $e^{-\alpha r^2}$ is multiplied by powers of *x, y* and *z,* and a constant for normalisation, so that:

$$\int_{all\ space} g^2 = 1 \tag{2.12}$$

Thus, c depends on α, *l, m* and *n*.Here are three representative gaussian functions (s, p_y and d_{xy} types, respectively):

$$g_s(\alpha,\vec{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

$$g_y(\alpha,\vec{r}) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} ye^{-\alpha r^2} \qquad (2.13)$$

$$g_{xy}(\alpha,\vec{r}) = \left(\frac{2048\alpha^7}{\pi^3}\right)^{1/4} xye^{-\alpha r^2}$$

Linear combinations of primitive gaussians like these are used to form the actual basis functions; the latter are called contracted gaussians and have the form:

$$\chi_\mu = \sum_p d_{\mu p} g_p \qquad (2.14)$$

Where the $d_{\mu p}$'s are fixed constants within a given basis set. Note that contracted functions are also normalised in common practice.

All of these constructions result in the following expansion for molecular orbitals:

$$\phi_i = \sum_\mu c_{\mu i}\chi_\mu = \sum_\mu c_{\mu i}\left(\sum_p d_{\mu p} g_p\right) \qquad (2.15)$$

The problem has now become how to solve for the set of molecular orbital expansion coefficients, $c_{\mu i}$

Hartree-Fock theory takes advantage of the variational principle, which says that for the ground state of any antisymmetric normalized function of the electronic coordinates, which we will denote Ξ , then the expectation value for the energy corresponding to Ξ will always be greater than the energy for the exact wavefunction:

$$E(\Xi) > E(\Psi) \qquad \Xi \neq \Psi \qquad (2.16)$$

In other words, the energy of the exact wavefunction serves as a lower bound on the energies calculated by any other normalized antisymmetric function. Thus the problem becomes one of finding the set of coefficients that minimize the energy of the resultant wavefunction [9].

The general strategy used by the SCF method (after initial setup steps) is as follows

- Evaluate the integrals. In a conventional algorithm, they are stored on disk and read in for each iteration. In a direct algorithm, integrals are computed a few at a time as the Fock matrix is formed.
- Form an initial guess for the molecular orbital coefficients, and construct the density matrix.
- Form the Fock matrix
- Solve for the density matrix.
- Test for convergence. If it fails, begin the next iteration. If it succeeds, go on to perform other parts of the calculation (such as population analysis).

2.2 Computational Methodology

The Computational Physics Gaussian package [3]is used to study the molecular properties of 2 Hydroxyanthracene. The name Gaussian comes from the fact that it uses Gaussian type basis functions. It is used for electronic and geometric structure optimization (single point calculation, geometry optimization, transition states and reaction path modeling); and molecular properties and vibrational analysis (IR, Raman, NMR vibrational frequencies and normal modes; electrostatic potential, electron density, multipole moments, population analysis, natural orbital analysis, magnetic shielding induced current densities, static and frequency-dependent polarizabilities and hyperpolarizabilities) using both DFT and ab initio methods.

Geometry optimization is done by locating both the minima and transition states on the potential surface of the molecular orbital. It can be optimized in Cartesian coordinates that are generated automatically from the input Cartesian coordinates. It also handles fixed constraints on distances, bond angles and dihedral angles in Cartesian or (where appropriate) internal coordinates. The process is iterative, with repeated calculations of energies and gradients and calculations or estimations of Hessian in every optimization cycle until convergence is attained

One of the most computationally demanding aspects of calculating free energy using electronic structure theory is the calculation of the vibrational energy and entropy contributions. The computational expense is incurred by the calculation of the matrix of second energy-derivatives (i.e. the Hessian or force constant matrix) which yields harmonic vibrational frequencies upon diagonalization.

The molecular structures and geometries of the organic semiconductor material 2 hydroxyanthraceneis completely optimized using ab- initio quantum mechanical calculations at the Restricted Hartree-Fock (RHF) level of theory without using any symmetry constraints. Geometry optimizations are performed using the ab-initio RHF method with 6-31G basis set. The structure is refined further using Density Functional Theory which is a cost effective method for inclusion of electron correlations with the three-parameter density functional generally known as Becke3LYP (B3LYP) [3-6]. At the first step, geometry optimizations are carried out then, the IR and Raman frequencies are calculated using the Hessian which is the matrix of second derivatives of the energy with respect to geometry.

Since the gas phase results are inadequate for describing the behavior of molecules in solutions, therefore the effect of solvating the molecule in bulk in ethanol is investigated. For this purpose the simplest Onsager reaction field model of the self-consistent reaction field (SCRF) theory is used with the 6-31G basis set. In this calculation the solute occupies a fixed spherical cavity within the solvent field. The electric dipole of the solute molecule induces a dipole in the medium and the electric field applied by the induced solvent dipole interacts with the molecular dipole and affects it.

3.0 Results and Discussion

Optimized Molecular Parameters of 2-Hydroxyanthracene

The optimized geometrical parameters in gas phase and ethanol for 2- Hydroxyanthracene molecule are listed in Tables 1 and 2 and the optimized molecular structure is shown in Figure 1. The changes in bond lengths and bond angles are seen to be similar to the behaviour of 1 Hydroxyanthracene [10]. An expansion of the molecule on inclusion of electron correlation is indicated in both molecules. Remarkably the bond lengths between C1 and O in 1 Hydroxyanthracene are the same as that between C2 and O in 2 Hydroxyanthracene [10]. This indicates that the OH bond on the benzene ring has same effect in both molecules. The change in bond length as one moves from gas phase to solution at both levels of theory is to the order of 0.001 Å. Unlike 1-hydroxyanthracene, the shortest bond C-H bond is R(13,22) with a bond length of 1.0707 Å and 1.0834 Å in gas phase at RHF and B3LYP levels of theory respectively. It is also worth noting that the O-H bond R(24,25) is longer than that in 1-hydroxyanthracene. This is remarkable because it indicates that the change in position for this O-H bond from position 1 to 2, reduces the strength of the bond. Thus, our computations predict a change in bond length of the O-H group as its position changes on the benzene rings.

The bond angles equally increase in solution. The least angles in solution are A(13,14,24), A(14,24,25), A(14,13,22), A(10,11,12), A(9,10,11), A(10,9,15) and A(4,5,19) with values ranging from 114^0 to 119^0 at both levels of theory (Table 2).

Table 1: Optimized Bond Lengths (Å) of 2-hydroxyanthracene molecule

Bond	RHF/6-31G		B3LYP/6-31G		Bond	RHF/6-31G		B3LYP/6-31G	
	Gas	Ethanol	Gas	Ethanol		Gas	Ethanol	Gas	Ethanol
R(1,2)	1.3532	1.3547	1.3745	1.376	R(9,10)	1.4274	1.4287	1.4493	1.4507
R(1,6)	1.4287	1.4307	1.4281	1.4299	R(9,15)	1.4348	1.4356	1.4318	1.4326
R(1,17)	1.0728	1.0751	1.0853	1.0876	R(10,11)	1.4361	1.4367	1.4346	1.4356
R(2,3)	1.433	1.4348	1.4319	1.4335	R(11,12)	1.0735	1.076	1.0859	1.0885
R(2,18)	1.074	1.0764	1.0865	1.0889	R(11,13)	1.349	1.3508	1.3699	1.3711
R(3,4)	1.4257	1.4275	1.4483	1.4498	R(13,14)	1.4273	1.4294	1.4277	1.4306
R(3,7)	1.3926	1.3937	1.4046	1.4059	R(13,22)	1.0707	1.0739	1.0834	1.0867
R(4,5)	1.4336	1.4354	1.4326	1.4343	R(14,15)	1.3504	1.3523	1.374	1.3762
R(4,8)	1.3932	1.3944	1.4048	1.4061	R(14,24)	1.3746	1.3735	1.3916	1.3878
R(5,6)	1.3533	1.3549	1.3746	1.3761	R(15,23)	1.0746	1.0765	1.0874	1.0892
R(5,19)	1.0738	1.0762	1.0865	1.0888	R(22,24)	2.5186	2.5334	2.5432	2.5535
R(6,20)	1.073	1.0753	1.0855	1.0878	R(24,25)	0.95	0.9675	0.9766	0.996
R(7,10)	1.3887	1.3905	1.4016	1.403	R(8,9)	1.3898	1.392	1.4033	1.4054
R(7,16)	1.0748	1.0772	1.0873	1.0897	R(8,21)	1.0746	1.0768	1.0871	1.0894

Table 2: Optimized Bond Angles (˚) of 2-hydroxyanthracene

Angle	RHF/6-31G		B3LYP/6-31G		Angle	RHF/6-31G		B3LYP/6-31G	
	Gas	Ethanol	Gas	Ethanol		Gas	Ethanol	Gas	Ethanol
A(2,1,6)	120.3147	120.3585	120.3268	120.358	A(10,9,15)	118.7896	118.9462	118.7792	118.9638
A(2,1,17)	120.4654	120.4711	120.276	120.2738	A(7,10,9)	119.4576	119.5953	119.3378	119.4906
A(6,1,17)	119.22	119.1705	119.3972	119.3682	A(7,10,11)	122.1163	121.9439	122.2375	122.0867
A(1,2,3)	120.9391	120.84	120.9779	120.8928	A(9,10,11)	118.4262	118.4609	118.4246	118.4227
A(1,2,18)	120.5918	120.73	120.5564	120.6512	A(10,11,12)	118.511	118.5585	118.4983	118.5627
A(3,2,18)	118.4691	118.4299	118.4657	118.456	A(10,11,13)	121.2783	121.104	121.3361	121.1687
A(2,3,4)	118.7723	118.8353	118.7248	118.7903	A(12,11,13)	120.2107	120.3375	120.1656	120.2686
A(2,3,7)	122.2296	122.0801	122.3577	122.232	A(11,13,14)	119.8142	119.9862	119.8265	120.0622
A(4,3,7)	118.9981	119.0846	118.9176	118.9777	A(11,13,22)	122.334	121.823	122.1219	121.6698
A(3,4,5)	118.4947	118.5235	118.4839	118.4994	A(14,13,22)	117.8518	118.1908	118.0516	118.268
A(5,4,8)	122.1445	122.0176	122.2912	122.1801	A(13,14,15)	121.4183	121.3531	121.2372	121.0737
A(4,5,6)	120.9383	120.8478	122.2912	120.9191	A(13,14,24)	114.6273	114.9299	114.9784	115.1901
A(4,5,19)	118.4738	118.4519	118.4721	118.472	A(15,14,24)	123.9543	123.7169	123.7844	123.7362
A(6,5,19)	120.5879	120.7003	120.5347	120.6089	A(9,15,14)	120.2734	120.1496	120.3963	120.3089
A(1,6,5)	120.5408	120.5949	120.4934	120.5404	A(9,15,23)	118.8069	119.1365	118.8102	119.1742
A(1,6,20)	119.1368	119.0842	119.3405	119.3034	A(14,15,23)	120.9197	120.7139	120.7935	120.5169
A(5,6,20)	120.3224	120.321	120.1661	120.1562	A(14,24,25)	114.8253	114.83	111.696	112.3201
A(3,7,10)	121.5996	121.4074	121.818	121.6492	A(10,7,16)	119.21	119.2812	119.0885	119.1584
A(3,7,16)	119.1904	119.3114	119.0935	119.1925	A(4,8,9)	121.5941	121.4336	121.8443	121.7156

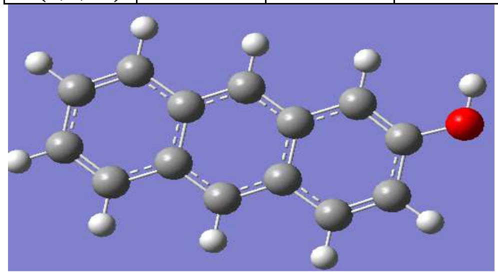


Figure 1: Optimized Structure of 2-Hydroxyanthracene

Dipole Moments, Quadrupole Moments and Energies

The predicted dipole moments (in Debye) for the moleculeat RHF level of theory is 1.3325 and 1.7119 in gas phase and ethanol respectively. At B3LYP level of theory, the dipole moments are respectively 1.1598 and 1.6359 in gas phase and ethanol.

The dipole moment of 2- Hydroxyanthracene increases significantly in solution and the magnitude of the dipole moment obtained at B3LYP/6-31G level is slightly lower as compared to the corresponding values of the dipole moment at RHF/6-31G level. Oxygen atoms are having the largest electronegativity, in this molecule and thus account for this charge asymmetry.The predicted dipole moments for 2-hydroxyanthracene in solution at both levels of theory are slightly less than that of 1-hydroxyanthracene. Thus, we note that the position of the O-H group also affects the dipole moment of the molecule [10]; and the choice of the molecule to use as an organic semi-conductor will thus depend on the preferred dipole moment required.

Quadrupole moments provide a second order approximation of the total electron distribution, providing at least a crude idea of its shape. One of the components being significantly larger than the others would represent an elongation of the sphere along that axis. If present, the off-axis components represent trans-axial distortion (stretching or compressing of the ellipsoid). The quadrupole moments for the molecule at different levels of theory is shown in Table 3

Table 3: Quadrupole moments (in Debye)

Orientation	RHF/6-31G		B3LYP/6-31G	
	Gas	Ethanol	Gas	Ethanol
XX	-85.5439	-83.3835	-83.0105	-79.9903
YY	-71.2033	-66.9084	-71.4339	-67.2698
ZZ	-94.6412	-95.0878	-91.7973	-92.2119

The molecule is predicted to be slightly elongated along the ZZ axis. The total electron distribution in order of magnitude beginning with the least is YY, XX, ZZ in gas phase and in ethanol at both levels of theory.

All frequency calculations include thermochemical analysis of the molecular system. By default, this analysis is carried out at 298.15 K and 1 atmosphere of pressure, using the principal isotope of each element type in the molecular system. Predicted total, electronic, translational, rotational and vibrational energies in kcal/mol for the three molecules both in gas phase and in ethanol is listed in Table 4.

Table 4: Predicted thermal energies (kcal/mol) in 2-Hydroxyanthracene

Energy	RHF/6-31G		B3LYP/6-31G	
	Gas	Ethanol	Gas	Ethanol
Total Energy	141.039	135.698	132.162	128.433
Electronic Energy	0.000	0.000	0.000	0.000
Translational Energy	0.889	0.889	0.889	0.889
Rotational Energy	0.889	0.889	0.889	0.889
Vibrational Energy	139.261	133.920	130.385	126.656

It is seen (Table 4) that the molecule is slightly more stable in gas phase. The difference in total energies from gaseous to solution phase is a bit larger when electron correlation is included. The highest vibrational energy for 2-hydroxyanthracene is 139.261kcal/mol in gas phase at RHF level of theory.

Charge Transfer and Polarizabilities

Within molecular system, atoms can be treated as a quantum mechanical system. On the basis of the topology of the electron density the atomic charges in the molecule can be explained**.** The electrostatic potential derived charges using the CHelpG scheme of Breneman at different atomic positions in gas phase and in ethanol of 2-Hydroxyanthracene molecule at RHF/6-31G and B3LYP/6-31G levels of theories is given in Table 5.

Table 5: Electrostatic Potential Derived Charges on different atomic positions

S/N	Atom	RHF/6-31G		B3LYP/6-31G		S/N	Atom	RHF/6-31G		B3LYP/6-31G	
		Gas	Ethanol	Gas	Ethanol			Gas	Ethanol	Gas	Ethanol
1	C	-0.089341	-0.084017	-0.063794	-0.073134	14	C	0.641306	0.379027	0.271125	0.293894
2	C	-0.223059	-0.265488	-0.197055	-0.224860	15	C	-0.573636	-0.416043	-0.322985	-0.350915
3	C	0.181562	0.218990	0.184169	0.187802	16	H	0.191259	0.235635	0.161651	0.189561
4	C	0.204406	0.220770	0.192423	0.189515	17	H	0.103834	0.122196	0.086818	0.103842
5	C	-0.215809	-0.249471	-0.186981	-0.210098	18	H	0.125665	0.150186	0.105709	0.127936
6	C	-0.091083	-0.125247	-0.096086	-0.109063	19	H	0.119873	0.150518	0.105124	0.127588
7	C	-0.384777	-0.473218	-0.364065	-0.396846	20	H	0.105708	0.132129	0.095222	0.112976
8	C	-0.452545	-0.488349	-0.387829	-0.413465	21	H	0.201449	0.238116	0.164464	0.193190
9	C	0.301727	0.259342	0.226976	0.225319	22	H	0.181026	0.206847	0.169723	0.173811
10	C	0.106692	0.162408	0.144438	0.142895	23	H	0.193544	0.201433	0.133572	0.167777
11	C	-0.161795	-0.190185	-0.143609	-0.163893	24	O	-0.812409	-0.757956	-0.588832	-0.658044
12	H	0.137969	0.139334	0.095300	0.117320	25	H	0.502745	0.500355	0.401454	0.463894
13	C	-0.294307	-0.267311	-0.186931	-0.217001						

The Mulliken population analysis partitions the charges among the atoms of the molecule by dividing orbital overlap evenly between two atoms. Whereas the electrostatic potential derived charges assign point charges to fit the computed electrostatic potential at a number of points on or near the Van Der Waal surface. Hence, it is appropriate to consider the charges calculated by CHelpG scheme of Breneman instead of Mulliken population analysis.

Polarizability refers to the way the electrons around an atom redistribute themselves in response to an electrical disturbance. We will consider the polarizability induced in the media as a result of the presence of the incident electric field, which may be described by the polarization vector $\vec{P}$. Assuming a linear response, and in the absence of any excitations in the medium, we have:

$$\vec{P}(\vec{r},t)=\varepsilon_0\cdot\vec{\chi}(\omega_I)\cdot\vec{E}_I(r,t) \tag{3.1}$$

where $\vec{\chi}(\omega_I)$ is the susceptibility tensor characterizing the macroscopic medium.

Furthermore, the presence of an excitation in the medium described by $X(\vec{r},t)$ results in a modulation effect of the wave functions and energy levels. From a macroscopic point of view, this modulation may be described by an additional contribution to the susceptibility tensor. Expanding $\vec{\chi}(\omega_I)$ in a series of Taylor up to first order we obtain:

$$\vec{\chi}=\vec{\chi}_0+\vec{\chi}'\cdot X \tag{3.2}$$

As a result, we obtain three contributions to the total polarizability:

$$\vec{P}_0=\varepsilon_0\cdot\vec{\chi}_0\cdot\vec{E}_I \tag{3.3}$$

$$\begin{aligned}\vec{P}_1=\vec{P}_{AS}+\vec{P}_S&=\sum_q\varepsilon_0\cdot\vec{\chi}'\cdot\left\{\vec{E}^0_I\cdot X^0(q,t)\cdot e^{i\left[(\vec{q}+\vec{k}_I)\cdot\vec{r}-\omega_{AS}\cdot t\right]}+c.c\right\}\\&+\sum_q\varepsilon_0\cdot\vec{\chi}'\cdot\left\{\vec{E}^0_I\cdot X^0(q,t)\cdot e^{i\left[(\vec{q}-\vec{k}_I)\cdot\vec{r}-\omega_S\cdot t\right]}+c.c\right\}\end{aligned} \tag{3.4}$$

where “c.c.” means “complex conjugate”.

The first contribution arises from the zero order susceptibility term, and gives rise to the Rayleigh elastic dispersion. The other two contributions arising from the coupling of the excitation and the electric field describe the scattered light that has changed its frequency. These two contributions are referred to as Stokes and Anti-Stokes radiation fields, and are described by their respective frequencies and wave-vectors:

$$\begin{aligned}\vec{K}_{AS}&=\vec{k}_I+\vec{q}\\\vec{K}_S&=\vec{k}_I-\vec{q}\\\omega_{AS}&=\omega_I+\Omega\\\omega_S&=\omega_I-\Omega\end{aligned} \tag{3.5}$$

The above equations describe the properties of the inelastically scattered light. In the Stokes process, the incident photon is scattered while a quantum of excitation with energy $\hbar\Omega$ is created in the crystal. In the Anti-Stokes process, a quantum of excitation is annihilated and therefore, the frequency of the scattered phonon increases [11].The polarizability tensor components of 2 Hydroxyanthracene molecules in gas phase and ethanol obtained at RHF/6-31G and B3LYP/6-31G levels of theory is listed in Table 6.

Table 6: Polarizabilities of 2-Hydroxyanthracene

Orientation	RHF/6-31G		B3LYP/6-31G	
	Gas	Ethanol	Gas	Ethanol
XX	245.507	376.550	280.996	417.898
XY	-4.018	-6.310	4.034	-5.743
YY	144.673	226.743	153.489	229.144
XZ	0.000	0.004	0.001	-0.011
YZ	0.000	-0.055	0.000	-0.046
ZZ	40.429	49.210	41.305	50.153

All the six polarizability tensor components (xx, xy, yy, xz, yz and zz) of 2-Hydroxyanthracene molecule increases significantly in going from gas phase to solution at both levels of theory . The change in polarizability tensors is more pronounced in solution than in the gas phase. This may be due to the fact that the polarity of the solvent and the dipole moments of the molecules are more in solution than in the gas phase. The polarizability along the off-diagonal axis xz, yz and xy is very minimal.

Vibrational Frequencies and Assignments

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared (IR) spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an ‘unknown’ with previously recorded reference spectra. The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. The vibrational frequency is usually expressed in cm^{-1}. Another important form of vibrational spectroscopy is Raman spectroscopy, which is complementary to infrared spectroscopy. The selection rules for

Raman spectroscopy are different to those for infrared spectroscopy, and in this case a net change in bond polarizability must be observed for a transition to be Raman active[12].

In this work, Gaussian software was used to predict the vibrational spectra of the three molecules in their ground states. These frequency calculations are valid only at stationary points on the potential energy surface, thus our computations were preformed on the optimized structures of the molecules. As 6-31G is the smallest basis set that gives satisfactory results for frequency calculations, it was used. Raw frequency calculations computed at the Hartree-Fock level contain known systematic errors due to the neglect of electron correlation, resulting to overestimates of about 10-12%. Therefore, it is usual to scale frequencies predicted at the HF level by an empirical factor of 0.8929. Use of this factor has been demonstrated to produce very good agreement with experiment for a wide range of systems. Our values in this study must be expected to deviate even a bit more from experiment because of the choice of a medium-sized basis set (6-31G)- around 15%. For B3LYP/6-31G a scale factor of 0.9613 is used [3]

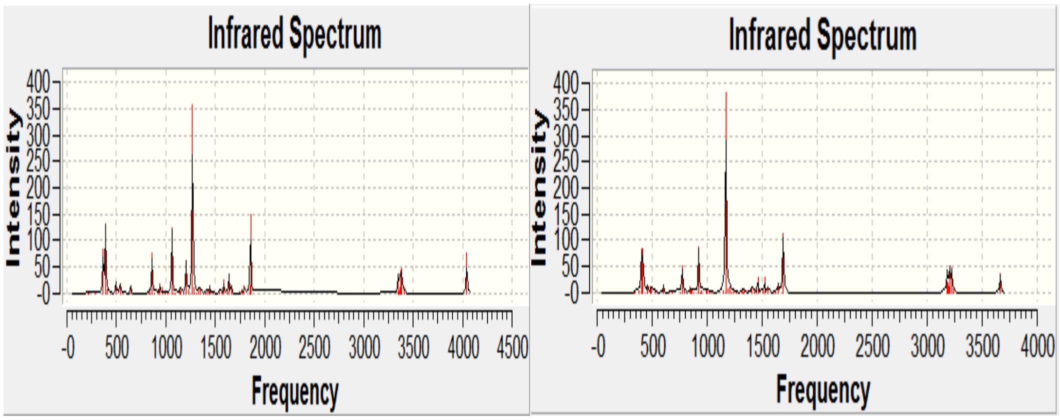
Some IR and Raman intense vibrational frequencies and their approximate descriptions for the molecules under study in gas phase and ethanol at RHF and B3LYP levels with 6-31+G basis set is presented in Tables 7 to 10. The frequencies reported are not scaled as is usually done in comparing the similar calculated frequency with observed frequency (as no experimental results were found for comparism). The B3LYP results show a significant lowering of the magnitudes of the calculated frequencies.

Table 7: Some IR Intense Vibrational Frequencies and their Approximate Description for 2-Hydroxyanthracene Molecule at RHF/6-31G Level of Theory

S/N	Gas	Ethanol	Approximate Description
1	366.282	187.127	O-H stretching out of plane
2	390.324	192.136	O-H stretching out of plane
3	861.318	426.384	C-H symmetric stretching of rings
4	1061.89	572.103	C-H symmetric stretching of rings
5	1205.2	597.537	C-C symmetric stretching of rings
6	1269.76	684.653	C-C symmetric stretching of rings
7	1856.69	976.074	C-C anti-symmetric stretching of rings
8	4043.38	3800.75	O-H stretching in plane

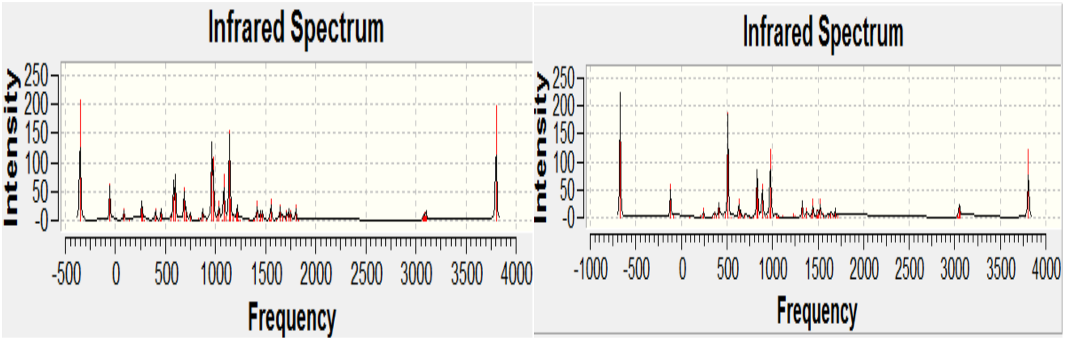
Table 8: Some IR Intense Vibrational Frequencies and their Approximate Description for 2-Hydroxyanthracene Molecule at B3LYP/6-31G Level of Theory

S/N	Gas	Ethanol	Approximate Description
1	402.755	321.637	O-H stretching out of plane
2	417.904	392.148	O-H stretching out of plane
3	773.521	630.39	C-H symmetric stretching of rings
4	923.711	725.26	C-H symmetric stretching of rings
5	1169.56	887.532	C-C anti-symmetric stretching in plane
6	1692.78	1560.25	C-C anti-symmetric stretching in plane



(a) RHF/6-31G (b) B3LYP/6-31G

Figure 2: IR Spectrum for 2-Hydroxyanthracene in Gas Phase



(a) RHF/6-31G (b) B3LYP/6-31G

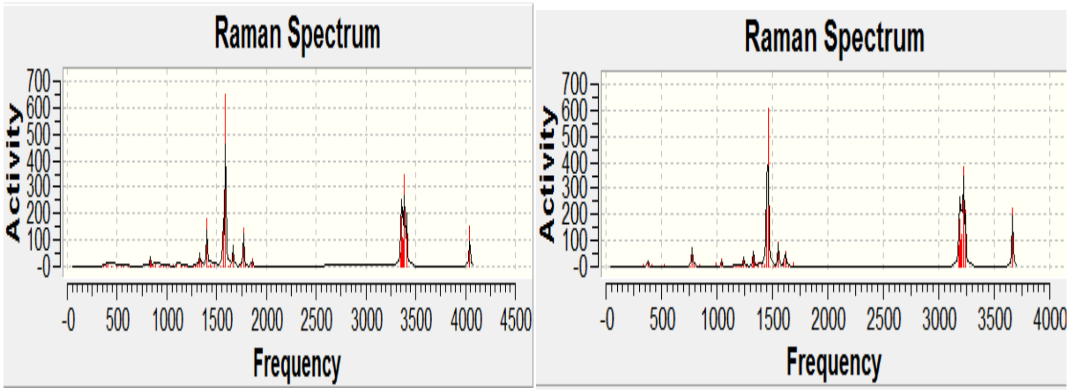
Figure 3: IR Spectrum for 2-Hydroxyanthracene in ethanol

Table 9: Some Raman Intense Vibrational Frequencies and their Approximate Description for 2-Hydroxyanthracene Molecule at RHF/6-31G Level of Theory

S/N	Gas	Ethanol	Approximate Description
1	1330.41	187.127	O-H stretching
2	1402.47	271.893	C-C anti-symmetric stretching in plane
3	1565.38	397.253	C-C anti-symmetric stretching in plane
4	1588.95	684.653	C-C anti-symmetric stretching in plane
5	1665.2	825.8	Ring breathing
6	1769.47	905.762	C-H symmetric stretching in plane
7	3355.5	1104.62	C-H anti-symmetric stretching in plane
8	3364.27	1332.51	C-H anti-symmetric stretching in plane
9	3371.75	1333.63	C-H symmetric stretching in plane
10	3387.42	1380.62	C-H symmetric stretching in plane
11	3408.9	1388.08	C-H symmetric stretching in plane
12	4043.38	3800.75	O-H stretching in plane

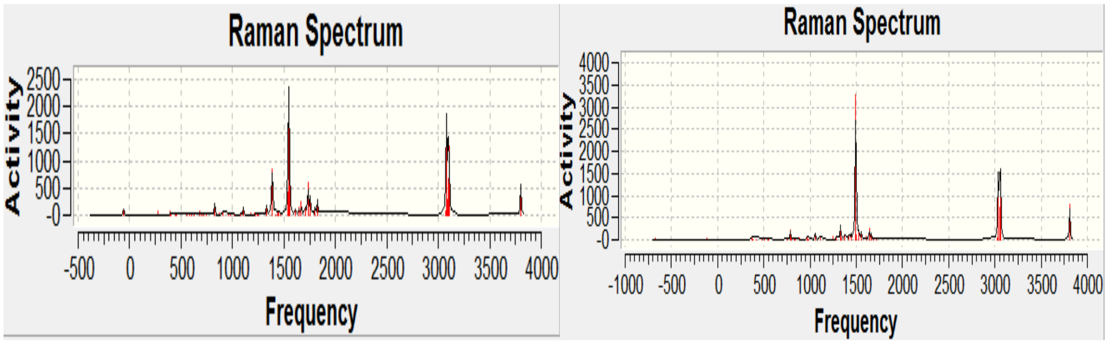
Table 10: Some Raman Intense Vibrational Frequencies and their Approximate Description for 2-Hydroxyanthracene Molecule at B3LYP/6-31G Level of Theory

S/N	Gas	Ethanol	Approximate Description
1	775.5	625.8	Ring breathing
2	1328.53	1100.31	C-C anti-symmetric stretching of rings
3	1447.64	1246.78	C-C anti-symmetric stretching of rings
4	1461.47	1275.44	C-C anti-symmetric stretching of rings
5	1553.92	1456.66	C-C anti-symmetric stretching of rings
6	1618.31	1520.11	C-C anti-symmetric stretching of rings
7	3184.62	2100.1	C-H anti-symmetric stretching of rings
8	3190.57	2315.37	C-H anti-symmetric stretching of rings
9	3199.42	2456.38	C-H anti-symmetric stretching of rings
10	3205.97	2731.80	C-H anti-symmetric stretching of rings
11	3221.68	2864.5	C-H symmetric stretching of rings
12	3238.7	2945.34	C-H anti-symmetric stretching of rings
13	3665.65	3108.6	O-H stretching in plane



(a) RHF/6-31G (b) B3LYP/6-31G

Figure 4: Raman Spectrum for 2-Hydroxyanthracene in Gas Phase



(a) RHF/6-31G (b) B3LYP/6-31G

Figure 5: Raman Spectrum for 2-Hydroxyanthracene in Ethanol

4.0 Conclusion

The practicability of the findings in this work is an encouraging factor. This work provides the fundamental basis for all computational and experimental studies on this molecule vis-a-vis its semi-conducting and opto-electric properties. Our study has exposed the molecular and electronic properties of 2 hydroxyanthracene for use in the fabrication of organic semi conductor devices.

To compliment this research work, the experimental part of this study can be undertaken to ascertain the accuracy of this computational technique. Also, this work can be done using other computational physics softwares and results compared with our results in this work.2-hydroxyanthracene can be studied in other environments to see the effect of these environments on their physical properties. Other solvents that can be considered include hexane, benzene, hydronaphthalenes, Carbon disulfide, Chloroform and other organic solvents.

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