


Density functional theory and *Ab Initio* Calculations of the Heats of Formation of Pyrrole and Furan Oligomers: Progress Report

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Abstract

Novel conducting polymers have attracted a great deal of attention among researchers because of their promising use as biosensors, organic semiconductors and other popular applications. Requirements of energy efficiency and environmental impact of energy combustion relate to fundamental quantities such as heats of formation of these compounds. However experiments measuring such quantities are not trivial and only few results have been reported. This lack of experimental information can be surmounted by resorting to reliable computational models which will also lead to expansion to new classes of compounds.

*In this study the heats of formation of polyfuran and polypyrrole were estimated computationally using ab initio G2(MP2) quantum mechanical protocol and density functional theory (B3LYP/6-311+G**) levels. Heats of formation of polyfuran and polypyrrole are calculated with an accuracy of better than ± 3 kcal/mol by using the total energy calculated.*

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Introduction

The Asian Committee for Future Colliders (ACFA) proposes the construction of the Joint Linear Collider (JLC), primarily to discover and study the Higgs boson, which is the only remaining unobserved particle in the particle spectrum of the Standard Model [15]. At the JLC, a vertex detector is needed in order to measure the particle tracks very close to the interaction point, thus allowing one to identify those tracks that do not come from the vertex [18]. Most vertex detectors seem to be made of inorganic semiconductors such as silicon (Si). However, when a large detector is needed, these cannot be made available because it is too difficult to make large Si crystals. It is also very expensive to make a large Si semiconductor detector [11].

In order to design a vertex detector with very much lower fabrication cost compared to Si, a collaboration between Niigata University of Japan and MSU-Iligan Institute of Technology of the Philippines has been conducting studies to explore the possibility of using conducting polymers as radiation sensors that could replace Si. Among the conjugated polymers, polythiophene (PT), polypyrrole (PPy), and polyaniline (PAni) have been extensively studied because they are the most attractive intrinsic conductive polymers [9,11]. Moreover, computer simulations were also conducted using DV-X α to estimate the band structure due to the impurities of PT, GEANT4 to study the efficiency of Pb-PAni and doped PT as biosensor and BIO-calorimeter, and Gaussian 94 [14] to approximate the energy band gap of intrinsic PT, PPy, PAni, polyacetylene (PA), and polyfuran (PF) [10,13,16]. Furthermore, structural studies of the α - α coupling of PPy and PT were also studied using *ab initio* evaluation [12, 17, 21, 22, 23].

To design an efficient vertex detector, it is also significant to study the heats of formation of these conducting polymers. The heats of formation are the fundamental quantities representing the energies of compounds in their standard states. However, these quantities are difficult to experimentally measure accurately, very time consuming, and require extreme care with regard to the design and conditions of the measurements [1].

In this study, the heats of formation in gas phase of pyrrole monomer, pyrrole dimer, furan monomer, and furan dimer were carried out using G2 (MP2) level. However, the lack of correlation energy in this approach sug-

gests that conjugated molecules such as PF and PPy, would probably not be well treated and, in general, the accuracy would be suspect. To accurately account for correlation, we use the DFT calculations, with every indication that this method is superior to the Hartree-Fock method, and can be extended to more diverse systems with a higher degree of confidence [1].

Computational Details

Ab initio molecular orbital theory is concerned with predicting the properties of atomic and molecular system [8] based on the solution of the Schrödinger equation which describes the wavefunction ψ of the particle:

$$H\psi = E\psi$$

E is the total energy of the particle and H represents the Hamiltonian operator for the system. For a closed shell configuration of paired in a many-electron system, the wavefunction $\psi_i(j)$ can be written as the slater determinant of the product of the spatial, $\Phi_i(j)$ and spin [$\alpha(j)$ or $\beta(j)$] components [29]:

$$\psi(1, 2, 3, \dots, n) = \left(\frac{1}{n!} \right)^{1/2} \begin{vmatrix} \Phi_1(1)\alpha(1) & \Phi_1(2)\alpha(2) & \dots & \Phi_1(n)\alpha(n) \\ \Phi_1(1)\beta(1) & \Phi_1(2)\beta(2) & \dots & \Phi_1(n)\alpha(n) \\ \Phi_2(1)\alpha(1) & \Phi_1(2)\alpha(2) & \dots & \vdots \\ \Phi_2(1)\beta(1) & \Phi_1(2)\beta(2) & \dots & \vdots \\ \Phi_3(1)\alpha(1) & \Phi_3(2)\alpha(2) & \dots & \vdots \\ \vdots & \vdots & \dots & \vdots \\ \vdots & \vdots & \dots & \vdots \\ \Phi_{n/2}(1)\beta(1) & \vdots & \dots & \Phi_{n/2}(n)\alpha(n) \end{vmatrix}$$

where $\Phi_i(j)$ denotes the i th spatial orbital containing the j th electron, and $\beta(j)$ and $\alpha(j)$ represent the electron spin functions for the j th electron

To estimate the energy and approximate the wavefunction of a known a Hamiltonian is to rely on the perturbation theory and variation theory. The perturbation theory is based upon dividing the Hamiltonian into two parts. The first is exactly soluble zeroth-order Hamiltonian $H^{(0)}$ which has known eigenfunctions and eigenvalues, and this defines the sum of the one-electron system from the Fock operators of the Hartree-Fock self consistent field (SCF) method. The second term gives the correlation energy of the ground state which is added as a perturbation to the exact Hamiltonian, thus:

$$H = H^{(0)} + \lambda V$$

such that $H^{(0)}$ is exactly soluble and λV is a perturbation applied to $H^{(0)}$, a correction which is assumed to be small in comparison to it. The variation theory is a way of assessing and improving guesses about the forms of the wavefunctions in complicated systems. The first step is to guess the form of a trial function and then the procedure shows how to optimize it.

The density functional theory (DFT) [8] is based on the Hohenberg-Kohn theorem [27] which states that the electron density can be used as the fundamental variable determining all atomic and molecular properties in the ground state. Furthermore, this can be performed in iterative manner. In Kohn-Sham [28] equation

$$\left[-\frac{1}{2} \nabla^2 + v_s(\vec{r}) \right] \varphi_i = \varepsilon_i \varphi_i$$

$v_s(\vec{r})$ explicitly includes all effects of electron-nuclear and electron-electron interaction such as attractive potential, classical Coulomb's repulsion within the electron density, and exchange correlation effects. Electron correlation is automatically incorporated via exchange-correlation functionals.

Following the work of Kohn and Sham, the approximate functionals employed by current DFT methods partition the electronic energy into several terms:

$$E = E^T + E^V + E^J + E^{XC}$$

where E^T is the kinetic energy term, E^V include terms describing the potential energy of the nuclear-electron attraction and the repulsion between pairs of nuclei, E^J is the electron-electron repulsion term and E^{XC} is the exchange-correlation term and includes the remaining part of the electron-electron interactions, it is usually divided into separate parts but actually corresponding to same-spin and spin interaction, respectively:

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho)$$

where E^X is the exchange functionals and E^C is the correlation functionals. Both components can be of two distinct types: local functionals depend only on the electron density ρ , while gradient-corrected functionals depend on both ρ and its gradient ∇_ρ .

The local exchange functional is virtually always defined as follow:

$$E_{LDA}^X = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}} d^3\vec{r}.$$

In 1988, Becke formulated a widely used gradient-corrected exchange functional based on the LDA exchange functional

$$E_{Becke88}^X = E_{LDA}^X - \gamma \int \frac{\rho^{\frac{4}{3}} x^2}{(1 + 6\gamma \sinh^{-1} x)} d^3\vec{r}$$

where $x = \rho^{\frac{1}{3}} |\nabla_\rho|$, γ is a parameter chosen to fit the known exchange energies.

Becke formulated functionals which include a mixture of Hartree-Fock and DFT exchange along with DFT correlation:

$$E_{B3LYP}^{XC} = E_{LDA}^X + C_o (E_{HF}^X - E_{LDA}^X) + C_x \Delta E_{B88}^X + C_c (E_{LYP}^C - E_{VWN3}^C)$$

where the parameter C_o allows an admixture of Hartree-Fock and LDA local exchange to be used, C_x is the Becke's gradient correlation to LDA exchange and C_c is the optionally corrected by the LYP correlation for the VWN3 local correlation functional.

Thermodynamic quantities such as entropy, energy, and heat capacity can be calculated from the translational, electronic, rotational, and vibrational motion. The partition function $q(V, T)$ [19] for the corresponding component of the total partition function is the starting point in each case:

1. Contributions from translation

The translational partition function is

$$q_t = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V.$$

where m is the mass of the particle, T is temperature, V is the volume, h is the Planck's constant, k_B is the Boltzmann's constant.

2. Contribution from electronic motion

The electronic partition function is

$$q_e = \omega_0 e^{-\epsilon_0/k_B T} + \omega_1 e^{-\epsilon_1/k_B T} + \omega_2 e^{-\epsilon_2/k_B T} + \dots$$

where ω is the degeneracy of the energy level, ϵ_n is the energy of the n -th level.

3. Contribution from rotational motion:

For a linear molecule, the rotational partition function is

$$q_r = \frac{1}{\sigma_r} \left(\frac{T}{\theta_r} \right)$$

where $\theta_r = \frac{h^2}{8\pi^2 Ik_B}$. I is the moment of inertia.

For the general case for a nonlinear polyatomic molecule, the rotational partition function is

$$q_r = \frac{\pi^{1/2}}{\sigma_r} \left(\frac{T^{3/2}}{(\theta_{r,x} \theta_{r,y} \theta_{r,z})^{1/2}} \right)$$

4. Contribution from vibrational motion

There are two ways to calculate the partition function, depending on where you choose the zero of energy to be: either the bottom of the inter-nuclear potential energy well, or the first vibrational level.

If you choose the zero reference point to be the bottom of the well, then the contribution to the partition function from a given vibrational mode is

$$q_{v,K} = \frac{e^{-\theta_{v,K}/2T}}{1 - e^{-\theta_{v,K}/T}}$$

and the overall vibrational partition function is

$$q_v = \prod_K \frac{e^{-\theta_{v,K}/2T}}{1 - e^{-\theta_{v,K}/T}}$$

For the first vibrational energy level to be zero of energy, then the partition function for each vibrational level is

$$q_{v,K} = \frac{1}{1 - e^{-\theta_{v,K}/T}}$$

and the overall vibrational partition function is:

$$q_v = \prod_K \frac{1}{1 - e^{-\theta_{v,K}/T}}$$

To calculate the enthalpies of formation first is to calculate the enthalpies of formation ($\Delta_f H^\circ(0K)$) of the species involved in the reaction. The second step is to calculate the enthalpies of formation of the species at 298K.

1. Calculate ($\Delta_f H^\circ(M, 0K)$) for each molecule:

$$\begin{aligned} (\Delta_f H^\circ(0K)) &= \sum_{\text{atoms}} x (\Delta_f H^\circ(X, 0K)) - \sum D_o(M) \\ &= \sum_{\text{atoms}} (\Delta_f H^\circ(X, 0K)) - (\sum_{\text{atoms}} x \epsilon_0(X) - \epsilon_0(M)) \end{aligned}$$

2. Calculate ($\Delta_f H^\circ(M, 298K)$) for each molecule:

$$\begin{aligned} (\Delta_f H^\circ(M, 298K)) &= (\Delta_f H^\circ(M, 0K)) + (H_M^\circ(298K) - H_M^\circ(0K)) - \\ &\sum_{\text{atoms}} x ((H_X^\circ(298K) - H_X^\circ(0K))). \end{aligned}$$

M stands for the molecule and X to represent each element which makes up M, and x will be the number of atoms of X and M. $\sum D_o(M)$ is the atomization energy of the molecule which can be readily calculated from the total energies of the molecule ($\epsilon_0(M)$), the zero point energy of the molecule ($\epsilon_{\text{ZPEZPE}}(M)$) and the constituent atoms:

$$\sum D_o(M) = \sum_{\text{atoms}} x \epsilon_0(X) - \epsilon_0(M),$$

$\Delta_f H^\circ(X, 0K)$ is the heats of formation of the atoms at 0K, $H_X^\circ(298K) - H_X^\circ(0K)$ is the enthalpy corrections for the atomic elements. These are used to convert the atomic heat of formation at 0K to those at 298.15K, and are given for the elements in their standard states. $H_M^\circ(298K) - H_M^\circ(0K)$ is the enthalpy correction for the molecule, for a molecule, this is $H_{\text{corr}}^\circ - \epsilon_{\text{ZPE}}(M)$, where H_{corr}° is the value printed out in the line labeled "Thermal correction to enthalpy" in Gaussian output.

All *ab initio* and density functional theory calculations were performed using Gaussian 94 [14] suite of quantum chemistry programs. Geometry optimizations and frequency calculations are done at the density functional theory level using Becke's Three Parameter Hybrid Method [24] and the correlation functional of Lee, Yang and Parr [25, 26] and 6-311+G** basis set (B3LYP/6-311+G**) and G2(MP2). The computations were carried out on a DEC Alpha Machine and PC workstations. Construction and visualization of molecular structures utilized the HyperChem™ [6] programs. Some interconversions of different file formats of molecular specifications into other forms of geometric input formats used the BABEL [7] program.

The first stage of the Gaussian calculations was using the G2(MP2) procedures. It involves geometry optimization at the HF/6-31G* level and calculation of the vibrational frequencies. The geometry is reoptimized at the MP2/6-31G* which is used as the reference geometry. An MP2/6-311+G was carried out which yielded the corresponding HF energy. The energy is then calculated at the QCISD(T)/6-311G** which automatically generated the MP2 value as an intermediate result. The energy difference between the QCISD(T) and MP2 is taken as an estimate of the higher-order correlation energy[14].

Results and Discussion

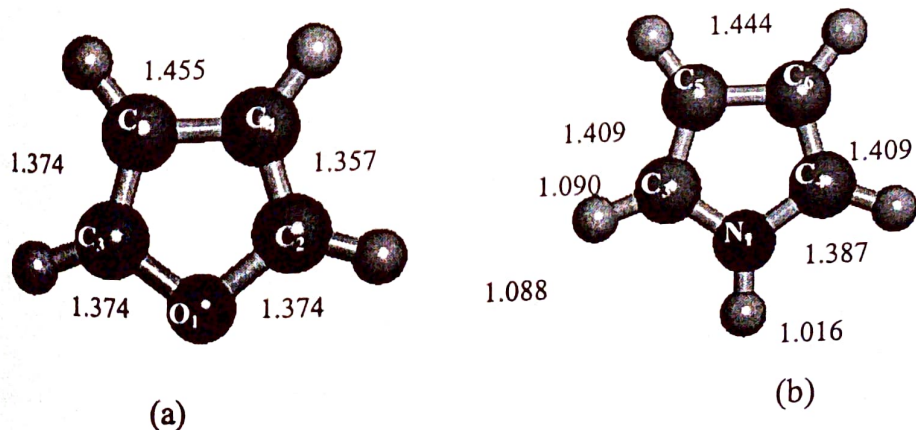


Figure 1. Structure of (a) furan and (b) pyrrole monomer optimized using 6-311+G** basis set.

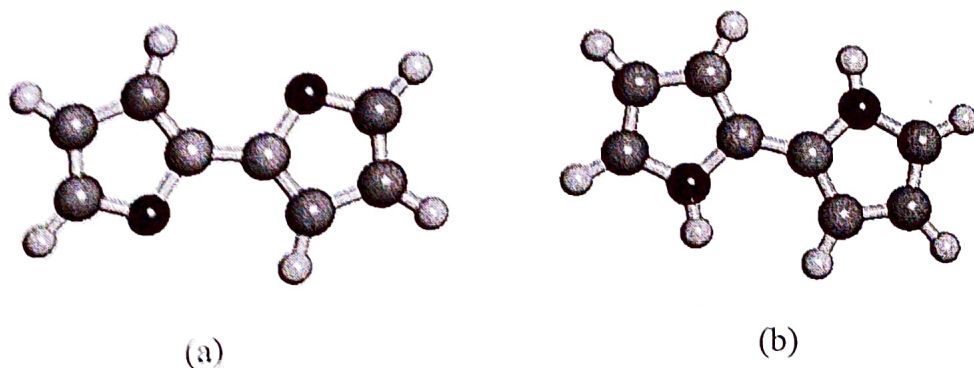


Figure 2. Structure of (a) furan dimer and (b) pyrrole dimer optimized using 6-311+G** basis set.

The calculated heats of formation determined by G2 (MP2) method are then given in Table 4. Table 3 gives the corresponding DFT calculated heat of formation data.

As expected, the *ab initio* G2 (MP2) calculations gave very reasonable results. We studied pyrrole, dipyrrole, furan, and difuran in gas phase. The experimental data for pyrrole and furan and also the results of G2(MP2) and dft calculations are compared. The G2(MP2) values agree with experiment of better than ± 1 kcal/mol for furan and better than ± 3 kcal/mol for pyrrole. Results for difuran and dipyrrole are still being calculated and are expected to be better than ± 3 kcal/mol as soon as experimental results are available.

Dft calculations using B3LYP/6-311+G** yielded 14.237 kcal/mol for furan and 10.868 kcal/mol for pyrrole. Dft calculation did not show good result for conjugated polymers for furan and pyrrole inspite of the introduction of the electron correlation energy. Calculations for difuran and dipyrrole were not pursued anymore since their corresponding monomers showed already deviations of greater than ± 5 kcal/mol and results will just follow.

Table 1. Calculated Energies of Compounds with zero point correction^a (G2(MP2) and B3LYP/6-311+G**).

Compound	Total Energy G2(MP2)	Total Energy (B3LYP/6-311+G**)
Furan	-229.627845	-230.018147
Difuran	on going	on going
Pyrrole	-209.774332	-209.148304
Dipyrrole	on going	on going
^a In Hartress		

Table 2. Calculated Energies of Atoms^a

element	G2 (MP2)	B3LYP/6-311+G**
H	-0.500	-0.502156
C	-37.783887	-37.857267
N	-54.516306	-54.600723
O	-74.978678	-75.089879
^a In Hartrees		

Table 3. Calculated Heats of Formation by B3LYP/6-311+G** Calculation^a

Compound	H_f^0 calc.	H_f^0 exp.	Δ calc. - exp.
Furan	5.924	-8.31 ^b	14.2374257 ^c
Difuran	on going	no exp. value	--
Pyrrole	36.728	25.86 ^b	10.868 ^c
Dipyrrole	on going	no exp. value	--

^a In kcal/mol at 298.15 K^b D. R. Lide, Ed., "CRC Handbook of Chemistry and Physics", CRC Press, Boca Raton, FL, 1998, 79th ed.^c R. V. Bantaculo, M. F. Fernandez et. al., "Ab Initio and DFT Calculation of the Heats of Formation of Polyfuran and Polypyrrole", Presented in the World Congress on Science and Technology and PhiLAAS 50th Anniversary, September 13-15, 2001, Manila Hotel, Manila.

Table 4. Calculated Heats of Formation by G2 (MP2) Calculation^a

Compound	H_f^0 calc.	Δ calc. -exp.
Furan	-7.535	0.775
Difuran	on going	--
Pyrrrole	28.525	2.665
Dipyrrole	on going	--

^a In kcal./mol at 298.15 K

Conclusion

Calculated *ab initio* results for heats of formation for furan and pyrrole are in good agreement with experiment of better than ± 3 kcal/mol and results for difuran and dipyrrole are expected to be better than ± 3 kcal/mol also. Further calculation using G2 basis set is recommended for better accuracy of the heats of formation. **Dft** calculations using B3LYP/6-311+G** have not shown in good agreement with experimental results especially for conjugated systems such as pyrrole and furan. Other levels of **dft** employing BLYP and B3P86 functionals are still to be explored in order to show comparison and investigate the reliability of **dft** results for conjugated systems.

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