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Thermodynamics properties of C_{24} and $C_{24}O_5$ cluster molecules using The Density Functional Theory

Taif Talib Khalaf*, Mohammed T. Hussein
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

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Abstract

Electronic characteristics density of state, density of bonds, and the thermodynamic characteristics (Gibbs Energy, Enthalpy, Entropy, and Heat Capacity) of coronene hydrogen bare C_{24} and reduced coronene oxide $C_{24}O_5$ were investigated with the variation of temperature between (298 – 398) K. The hybrid functional B3LYP (Becke, 3-parameters, Lee-Yang-Parr) with 6-311G** basis sets was employed in Density Functional Theory (DFT). It was found that the value of the energy gap of coronene hydrogen bare C_{24} was 3.5 eV, while it decreased for reduced coronene oxide $C_{24}O_5$ to 1.38 eV due to adding levels inside the energy gap. The theoretical values of bond length were 1.38 Å for the C=C bond and 1.22 Å for the C=O bond, which were in good agreement with experimental results. An exergonic reaction was indicated by a decrease in the Gibbs energy (in a negative sign) as the temperature rise. Entropy, heat capacity, and enthalpy all increased in value with temperature.

Keywords: Coronene Hydrogen bare, reduced coronene oxide, Thermodynamics characteristics, Density Functional theory

الخصائص الحرارية للجزيئات C_{24} و $C_{24}O_5$ باستخدام نظرية دالية الكثافة

طيف طالب خلف*, محمد تقي حسين
قسم الفيزياء, كلية العلوم, جامعة بغداد, بغداد, العراق

الخلاصة

تمت دراسة الخصائص الالكترونية مثل (كثافة الحالة وكثافة الاواصر) بالاضافة الى الخصائص الحرارية المتضمنة (طاقة جيبس, الانثالبي, الانتروبي والسعة الحرارية) للكورونين منزوع الهيدروجين C_{24} والكورونين اوكسايد المختزل $C_{24}O_5$ مع تغير درجة الحرارة بين K (298 – 398). تم استخدام نظرية دالية الكثافة مع الدالية الهجينة B3LYP (Becke, 3-parameters, Lee –Yang-Parr) ومجموعة الاساس 6-311G**. وجد أن قيمة فجوة الطاقة للكورونين منزوع الهيدروجين C_{24} تساوي 3.5 eV بينما تقل بالنسبة للكورونين اوكسايد المختزل $C_{24}O_5$ لتصبح 1.38 eV وذلك بسبب اضافة مستويات داخل فجوة الطاقة. القيم النظرية لطول الاصرة كانت A° (1.38 C=C and 1.22 C=O) والتي كانت متفقة بشكل

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*Email: taif.taleb1604a@sc.uobaghdad.edu.iq

جيد مع النتائج العملية. تتناقص طاقة جيبس في (اشارة سالبة) مع زيادة درجة الحرارة مما يدل على وجود تفاعل باعث للطاقة, في حين ان قيمة الانثالبي والانتروبي والسعة الحرارية تزداد كدالة لدرجة الحرارة.

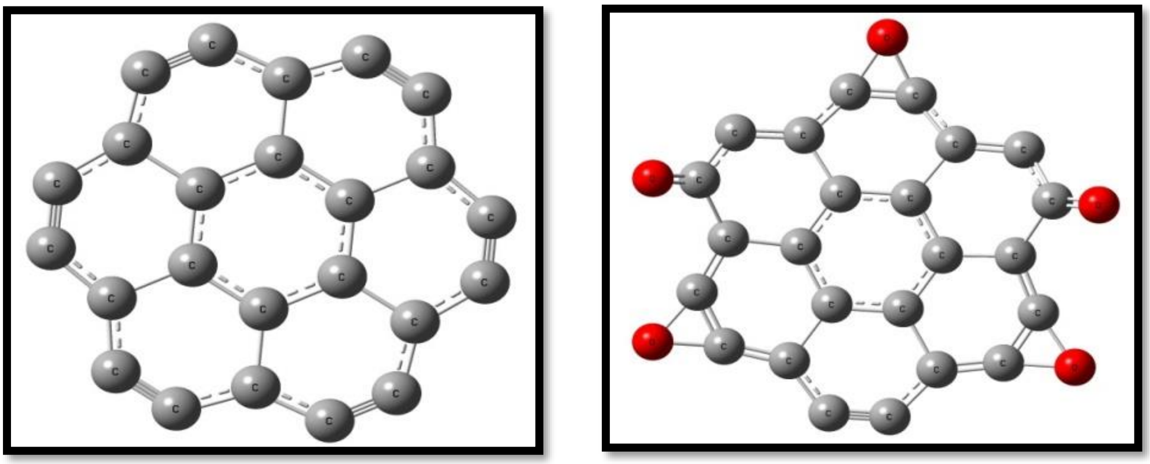
1. Introduction

The polycyclic aromatic hydrocarbon (PAH) molecule coronene is distinguished by its distinct super benzene molecule. It is made up of six benzene rings fused together in a peri arrangement. The electrons in coronene can be fully delocalized among the benzene rings because of this unique configuration. It is found in sedimentary rocks in nature and is also detectable during the hydrocracking process used in petroleum refining [1]. The synthesis of many π-conjugated organic compounds has drawn substantial attention to the sp^2 carbon structure [2,3]. Since coronene molecules have a unique planar electrical structure, they can stack firmly, facilitating effective self-assembly and enhanced electron mobility [4]. It is thought that graphene and carbon nanotubes, two materials with extraordinary electron conductivity, are extensions of the coronene structure. Several efforts have been undertaken to synthesize coronene derivatives with different electrical and electronic properties [5,6]. Graphene was initially used in electronic devices, with an emphasis on its electrical characteristics [7]. Numerous fields have used graphene, including conducting electrodes, gas detection, supercapacitors, and energy storage systems like lithium-ion batteries [8]. Previous theoretical studies used coronene ($C_{24}H_{12}$) as a model to examine how oxygenated groups affect the spectral and structural properties of graphene oxide (GO). Geometry optimization, vibrational IR, and Raman spectra of functionalized coronene molecules are performed. The results provide valuable data for the analysis of IR and Raman spectra of GO, revealing more detailed structural effects [9]. Jabbar examined and used geometrical optimization to analyze the molecules of coronene and coronene-Y (Y = Al, B, C, Ga, In, O). It was discovered that new bonds were formed, the ionization potential was decreased, but the electron affinity was raised when Y atoms interacted with coronene. In coronene-Y, coronene functioned as a donor; but coronene-boron and carbon exhibited an energy gap akin to semiconductors. The most polarizable molecule was coronene-In, whereas coronene-carbon and coronene-oxygen were anti-ferromagnetic molecules [10]. In our previous study, the spectroscopic characteristics, like IR Spectra and Raman Spectra as well as the electronic characteristics, such as band gap (HOMO and LUMO Levels) of coronene ($C_{24}H_{12}$) after removing hydrogen atoms and substituting it with oxygen to get reduced coronene oxide ($C_{24}O$- $C_{24}O_5$), were studied [11]. Abdulradha et al. investigated the interaction between $C_{24}O_5$ and nitrogen dioxide as a gas sensor using density functional theory and Gaussian 09W software [12].

The current work explores the effect of temperature change and oxygen atoms on the electronic and thermodynamic properties of coronene-hydrogen bare (C_{24}) and reduce coronene oxide $C_{24}O_5$; this is an extremely significant nanostructure in optoelectronic devices.

2. Computation

It is the Density Functional Theory (DFT) that is most dependable for understanding the properties and structures of molecules and nanostructures. DFT is well-known for having a strong fit for experimental data. B3LYP is a hybrid function of the DFT that is most frequently utilized [13-18]. It was discovered that B3LYP outperformed other features that encouraged its use. In the hybrid functional B3LYP, HF exchange is coupled with energy from exchange-correlation sources [19]. In this study, 6-311G** basis set was utilized for light atoms, such as carbon (C) and oxygen (O) [20, 21]. The vibration frequency was adjusted using a scaling factor of 0.967 [22]. All calculations (Electronic and thermodynamics properties) were investigated using two software programs: Gaussian View 05 for molecular design and Gaussian 09W for theoretical calculations [23], as shown in Figure 1.



(a) **(b)**

Figure 1: Geometrical optimization of (a) coronene hydrogen bare C_{24} and (b) reduced coronene oxide $C_{24}O_5$.

3. Results and Discussion

3.1 Electronic properties

Figure 2 illustrates the density of state of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) for (a) coronene hydrogen bare C_{24} and (b) reduced coronene oxide $C_{24}O_5$ after geometrical optimization.

Often referred to as the band gap, is the difference in energy levels between (LUMO) and (HOMO) [24].

$$Eg = |LUMO - HOMO| \tag{1}$$

The energy band gap of coronene hydrogen bare C_{24} was determined to be 3.5 eV, primarily attributed to the strong symmetry of the coronene nanostructure. The band gap of quasiparticles is significantly influenced by both the Coulomb interaction and the quantum confinement geometry [25], this energy gap value of coronene hydrogen bare (3.5 eV) was compared with the practical energy gap value of Graphene (G) is (1.4) eV [26]. The value of the energy gap of reduced coronene oxide ($C_{24}O_5$) was less, becoming 1.38 eV due to the broken symmetry and the addition of levels within the energy gap.This value of energy gap of reduced graphene oxide (1.38 eV) was compared with experimental values of a range (1 - 2.2) eV for graphene oxide (GO) [27, 28].

Theoretical bond density values for coronene hydrogen bare C_{24} and reduced coronene oxide $C_{24}O_5$ as a function of bond length are shown in Figure 3. The theoretical value of the C=C bond length for coronene hydrogen bare C_{24} was 1.38 Å. For reduced coronene oxide $C_{24}O_5$, the C=C and C=O bond lengths were 1.34 and 1.22 Å, respectively. These values are in good agreement with the experimental results of 1.34 Å and 1.23 Å, respectively [29].

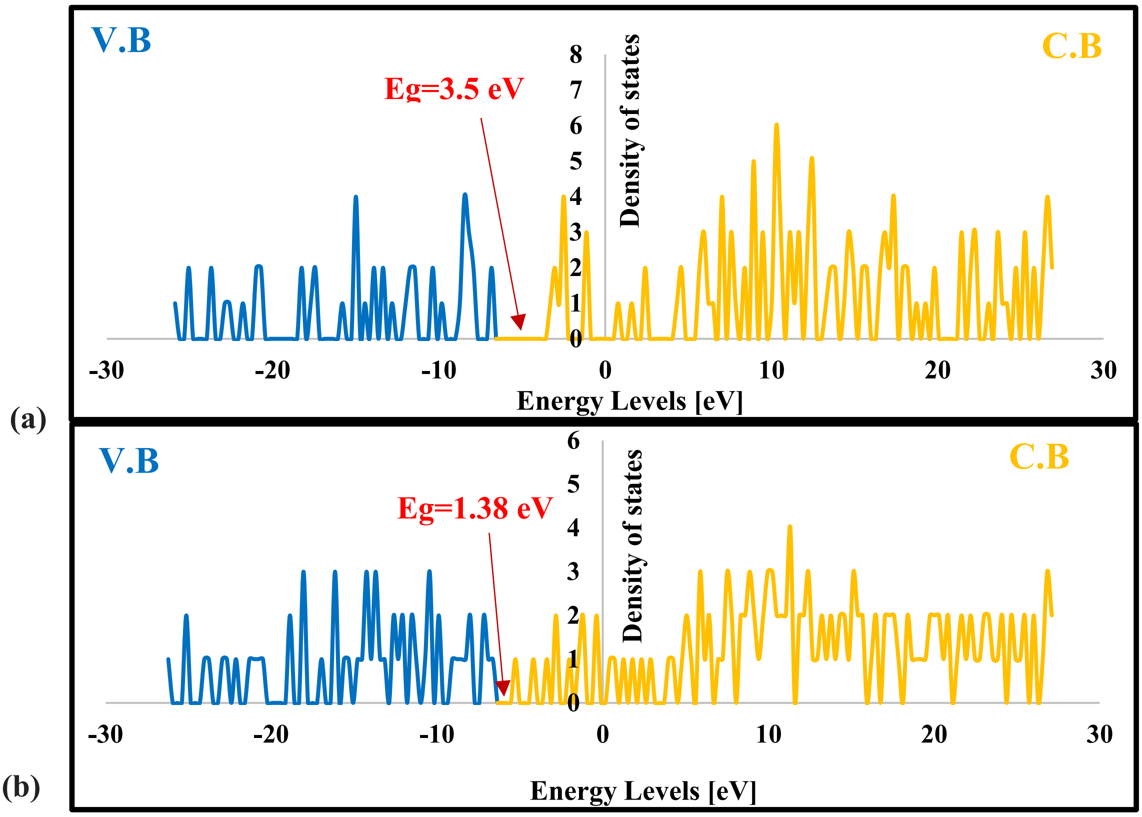


Figure -2: Density of states according to energy levels for (a) Coronene Hydrogen bare C_{24} and (b) reduced coronene oxide $C_{24}O_5$

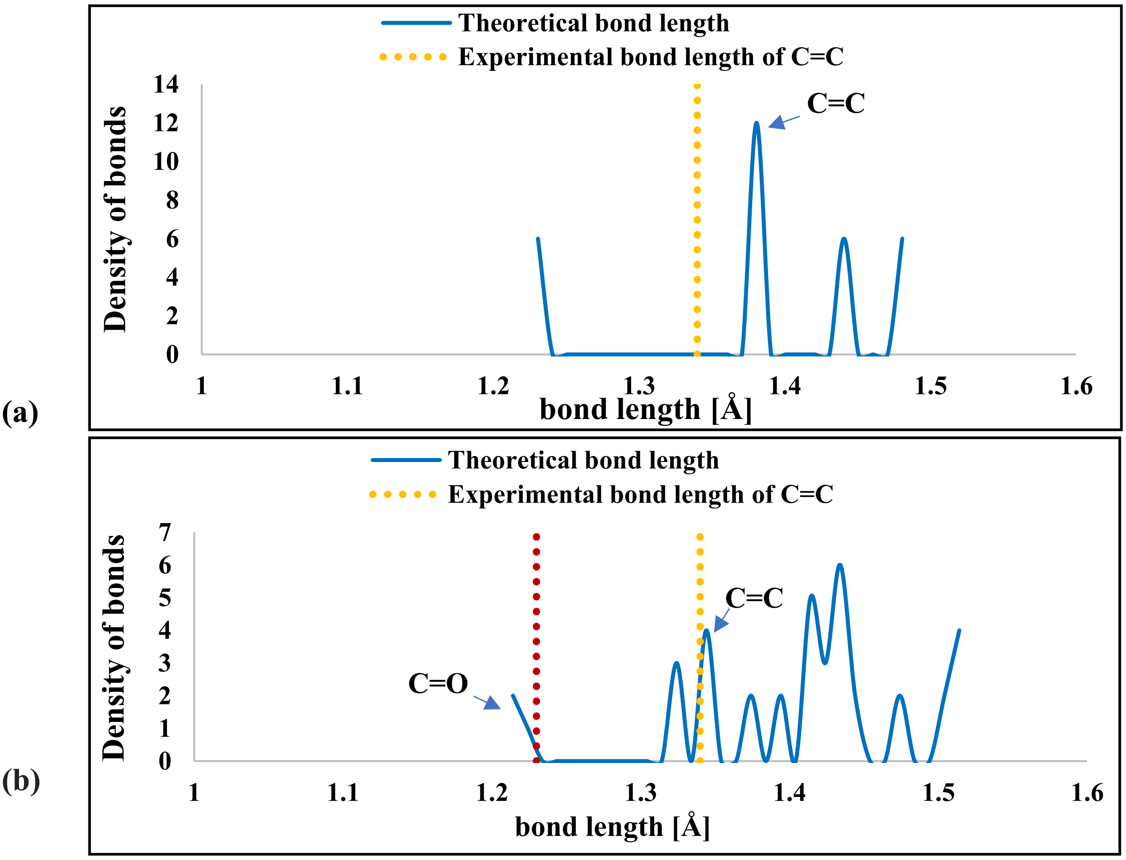


Figure 3: Density of bonds of (a) coronene hydrogen bare C_{24}, (b) reduced coronene oxide $C_{24}O_5$ according to bond length

3.2 Thermodynamics properties

Figure 4 shows the thermodynamic characteristics of Gibbs energy, enthalpy, entropy, and heat capacity for reduced coronene oxide $C_{24}O_5$ at different temperatures from (298 - 398) K. It emerged that when the temperature rise, Gibbs energy decreased (negative sign), according to Eq. (2) [30,31], which indicates an exergonic reaction. It was also observed that as the temperature rise, the enthalpy values rise as well. However, when temperatures rise, so did entropy, which causes the system to become more disordered, in addition, the temperature of the material increases due to the increase in heat capacity. Table 1 shows the variation in the thermodynamic properties of coronene hydrogen bare C_{24} and reduced coronene oxide $C_{24}O_5$ at room temperature 298 K.

$$\Delta G = \Delta H - \Delta S.T \tag{2}$$

$$\Delta H = \Delta U + \Delta PV \tag{3}$$

$$\Delta S = \frac{Q}{T} \tag{4}$$

$$C = \frac{Q}{m\,\Delta T} \tag{5}$$

where: ΔG is Gibbs energy, ΔH is enthalpy, ΔS is entropy, T is temperature, U is internal energy, P is pressure, V is volume, C is heat capacity, Q is the amount of heat, m is mass, and ΔT is the change in temperature.

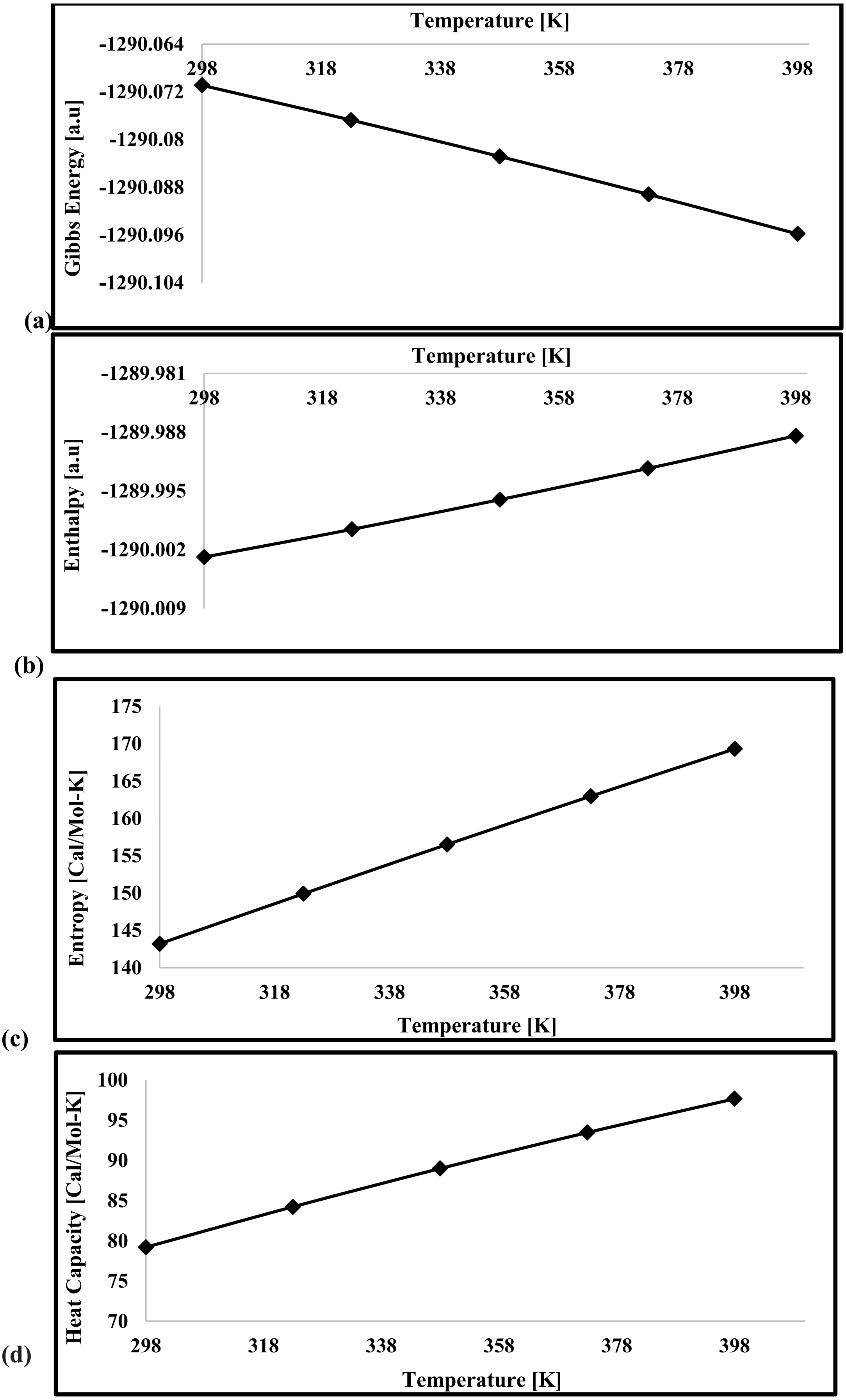


Figure 4: The thermodynamics properties of reduce coronene oxide $C_{24}O_5$ for (a) Gibbs energy, (b) Enthalpy, (c) Entropy and (d) Heat Capacity at different temperatures.

Table 1: The values of the thermodynamic properties of coronene hydrogen bare C_{24} and reduced coronene oxide $C_{24}O_5$ at room temperature 298 K

Thermodynamics properties	C_{24}	$C_{24}O_5$
Gibbs Energy (a.u)	**-913.979**	**-1290.070**
Enthalpy (a.u)	**-913.924**	**-1290.002**
Entropy (Cal/Mol-K)	**117.256**	**143.201**
Heat Capacity (Cal/Mol-K)	**61.926**	**79.197**

4. Conclusions

The energy gap of the coronene hydrogen bare C_{24} was high due to the high symmetry and the quantum confinement effect, as well as the Coulomb interaction. It was found that the energy gap decreased with the substituting of oxygen atoms instead of hydrogen of coronene; this is due to broken symmetry and adding levels inside of the energy gap. Two geometrical bond lengths were determined; the longest bonds were C = C, followed by the shortest bonds, C = O. It was noticed that the values of Gibbs energy decreased (in negative sign) with increased temperature, indicating an exergonic reaction.

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