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Investigation of the Electrical Conductivity of Pernigranilin with Carbon Monoxide and Nitrogen Monoxide Doping

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Abstract
In a wide range from electronic elements to solar panel systems, organic semiconductors seem to replace silicon-based structures. Aim: The aim of this research is to examine the electrical conductivity properties of pernigraniline, which has insulating properties, by doping. Methodology: For this purpose, geometry and energy optimization were performed with the MMFF94 algorithm by forming a 4-ringed pernigraniline molecule in a unit cell with Avogadro. After producing the crystallographic information file for the 4-ringed pernigraniline molecule optimized with the Burai program, (1) vc-relax, (2) self-consistent field, and (3) band optimization was performed, respectively, using the Quantum Espresso program. Numerical calculations regarding the current state of the 4-ringed pernigraniline were performed in TÜBİTAK Ulakbim, High Performance and Grid Computation Center (TRUBA resources). The numerical calculations reported in this paper were partially performed at TUBITAK Ulakbim, High Performance and Grid Computing Center (TRUBA resources). Findings: LUMO -2.9479 eV, Homo -1.7895 eV, Fermi -2.3737 eV and Band Gap 1.1584 eV were obtained for Pani-PB. In addition, -2.1792 eV for Fermi energy, -2.4692 eV for LUMO level, -1.8768 eV for Homo level and 0.5924 eV for bad gap were found for Pani PB-CO dopped, respectively. By performing similar procedures, Fermi energy -2.0175 eV, LUMO -2.1085eV, HOMO -1.9263 eV and band gap 0.1822 eV for PANI PB-NO dopped, respectively. Result: According to the results obtained, the semiconducting property of pernigraniline material resulting from doping with NO gave better results than doping with CO.
Keywords: Pernigraniline, Conductivity, Doping, Semiconductor, Energy Band Gap.

Introduction

Reducing industrial waste, which does not mix with nature and therefore creates environmental pollution, has become an important priority. In this research, polymer-based semiconductor structures, which will replace the silicon-based electronic products that pollute the environment and will pollute the nature less, have been examined. As it is known, silicon-based semiconductor materials have been used in many structures such as electronic elements (diode, transistor, FET, MOSFET, etc.), integrated circuits or solar panels since the 1950s. On the other

hand, semiconductor polymers are used in a wide range of fields from optoelectronics to materials science (the various electrochemical biosensors and sensing systems)[1].

It is known that silicon-based electronic industrial products pollute the nature. It is known that silicon-based electronic industrial products pollute the nature. It is seen that environmentally friendly polymer-based organic electronic products will soon replace silicon-based electronic products.

Polyanilines attract great attention due to their easy synthesis, cost advantage, good thermal resistance, easy preparation in organic solvents by chemical and electrochemical methods, and use in various commercial and technological applications such as electronics, pharmaceuticals and corrosion inhibitors. Conjugated conductive polymers mainly include polyaniline (PANI), polythiophene (PTH), polypyrrole (PPY) and their products. The properties of PANI have been well studied and PANI shows magnetic, electrical, Redox, antioxidant, anti-corrosion, charge-discharge, capacitive, sensing properties [2].

The most widely known types of polyaniline are called aniline black or emeraldine. Although these organic materials have been known for about 100 years, their structures have not been fully explained. Today, conductive organic structures can be synthesized by chemical or electrochemical means. The conducting polyaniline is called the emeraldine salt. If the emeraldine salt is andoped with a suitable base, it loses its conductivity and turns into emeraldine base, that is, nigranil [3].

Electronic properties of polyaniline, oxidation calculations of Leukoemeraldin, Emeraldin, Protoemeraldin, Nigranilin and Pernigranilin groups can be made by density functional theory (DFT). When the band structure of the organic structure is examined in terms of charge density, permeability and electric current, it has been observed that the “Leukoemeraldin”, “Pernigranilin”, “Protoemeraldin”, “Emeraldin” and “Nigranilin” groups of polymers show metallic properties [4].

Polyaniline (PANI) group organic materials are sometimes introduced as superconductors. Because this polymer group has electrical conductivity, environmental stability and unique redox properties with chain heteroatoms [5].

There are few studies on Pernigranilin in the literature and its electronic properties are not well known. Therefore, to make the research unique, how the insulator Pernigranil can be a semiconductor is discussed in the solid crystal phase. The conductivity properties of pernigranil in the solid phase were also investigated and its semiconducting properties were investigated by doping with CO and NO.

Methodology

In this study, numerical calculations regarding the current state of the 4-ringed pernigranil molecule and its changing electrical properties after doping with NO and CO were performed in TÜBİTAK ULAKBİM, high performance and grid calculation center (TRUBA resources).

Electronic properties of pernigranil were analyzed with Quantum Espresso software. For the calculations, pseudopotential files were used according to Perdew–Burke–Ernzerhof's (PBE) Generalized Gradient Approach (GGA). The convergence threshold on the forces for ionic minimization is 1.10^{-3} a.u., and the total energy convergence threshold is 1.10^{-4} a.u. geometry optimization was performed using the BFGS semi-newton algorithm. However, the SCF convergence threshold used to minimize the estimated energy error was determined as 1.10^{-5}, and the kinetic energy cut-off value for wave functions was taken as 40 Ry and for charge density as 320 Ry. A Monkhorst-Pack network is constructed for the Brillouin region in k space of size $1 \times 6 \times 6$.

Findings

Optimized and doped with Avagadro 1.2.0 pernigraniline molecules are shown in Fig. 1.

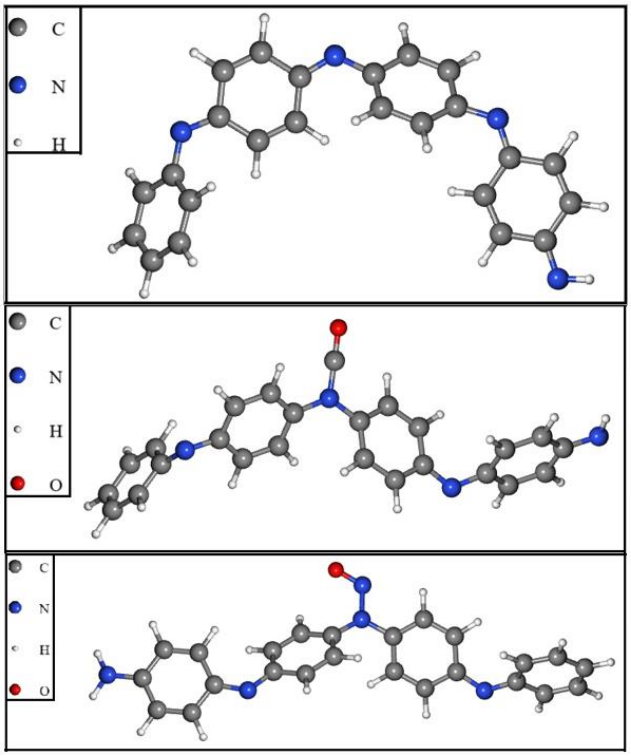


Figure 1. Optimized and Doped Pernigraniline Molecules (a) 4-PANI PB, (b) 4-PANI PB-CO, (c) 4-PANI PB-NO

With the help of the Quantum Espresso program, the unit cell and molecular geometry must first be optimized in order to find the electronic band structure and calculate the E_{GAP}. For this reason, the total energy optimization obtained by the VC-Relax process is shown in Fig. 2. It was observed that the energy optimization converged from -400,85 Ry to -400,89 Ry in 125 iterations.

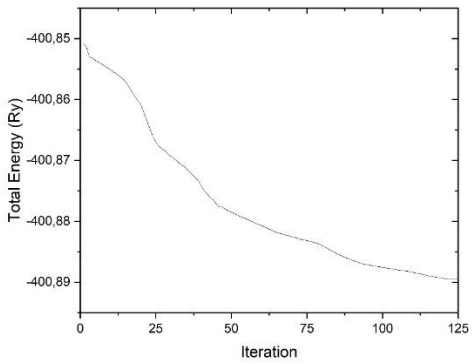


Figure 2: Total Energy Variation of 4-PANI-PB

The unit cell volume change to pernigraniline by the VC-Relax is shown in Fig.3. After about 20 iterations, the unit cell volume changed exponentially to 1380 Ang^3 up to 125 iterations.

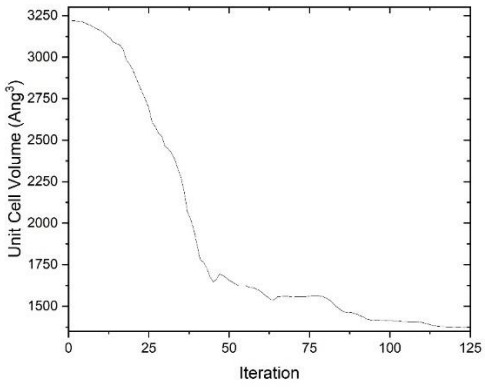


Figure-3 Unit Cell Volume Change of 4PANI-PB

Unit cell density variation is an important issue in terms of energy optimization. With the VC-Relax process, the unit cell density change was obtained as seen in Fig.4.

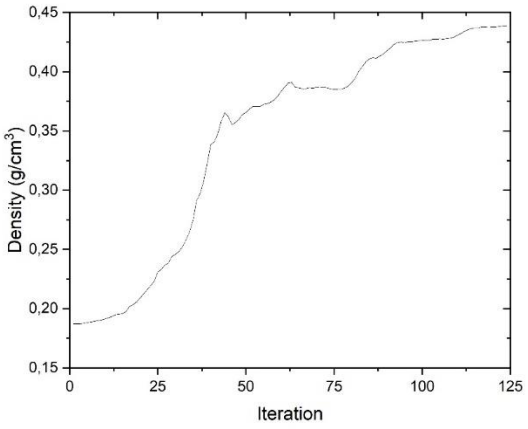


Figure 4 Unit Cell Density Variation of 4PANI-PB

After the VC-Relax process, iteration with SCF optimization is required. The graph of 4 PANI PB data obtained by SCF optimization in this study is presented in Fig.5. As can be seen from the graph in Fig.5, it has been determined that the total energy has changed exponentially since the first iteration and converged at the end of 10 iterations to -400,8 Ry. In this case, the resulting energy Fermi level is -2.3737 eV.

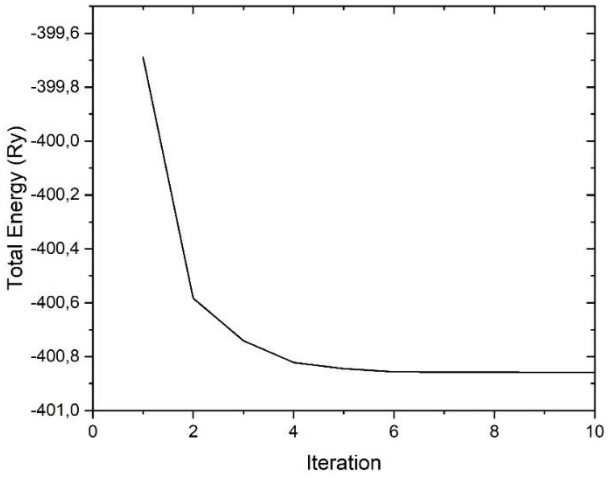


Figure-5 Total energy optimization obtained by the 4PANI PB SCF process

After the optimization was achieved with the SCF process, the energy band gap calculation was made. The variation of the energy band values with high symmetry points and the energy fermi level are shown in Fig. 6. The EGAP calculation is made from the difference between the lowest energy band (LUMO) above the Fermi energy and the highest energy band (HOMO) below the Fermi energy level. The data obtained are LUMO -2.9479 eV, HOMO -1.7895 eV, Fermi -2.3737 eV and band gap 1.1584 eV, respectively.

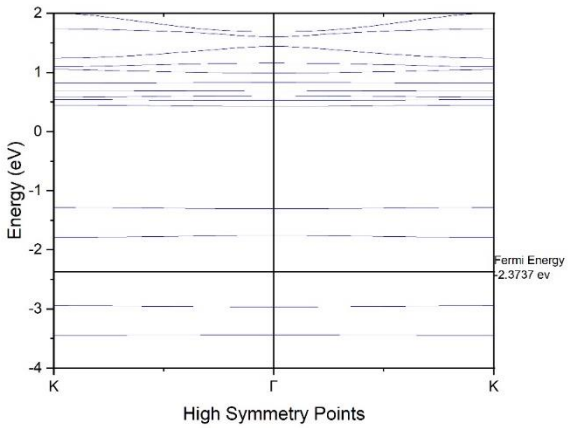
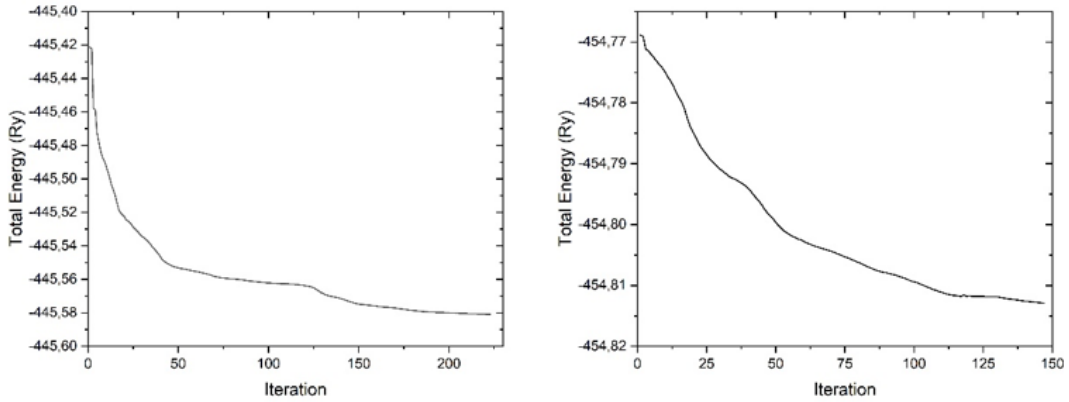


Figure-6 Energy Band Values of 4 PANI PB

Dopping with CO and NO

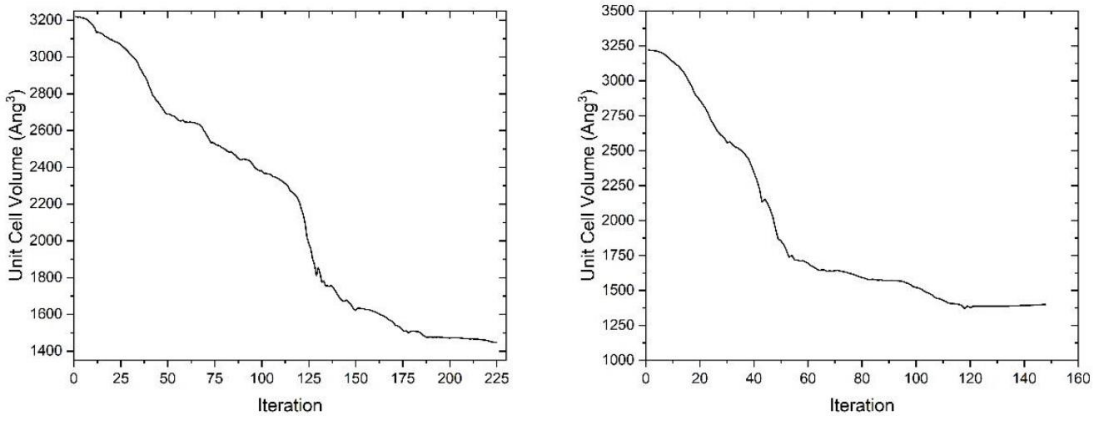
The total energy optimization obtained by the VC-Relax process is shown in Fig.7. While the convergence was achieved in 225 iterations in doping with CO to -445,58 Ry. With energy optimization, convergence was achieved in doping with NO to -454,815 Ry. In 150 iterations.



(a) (b)

Figure-7 Change of Total Energy (a) 4PANI PB-CO, (b) 4PANI PB-NO

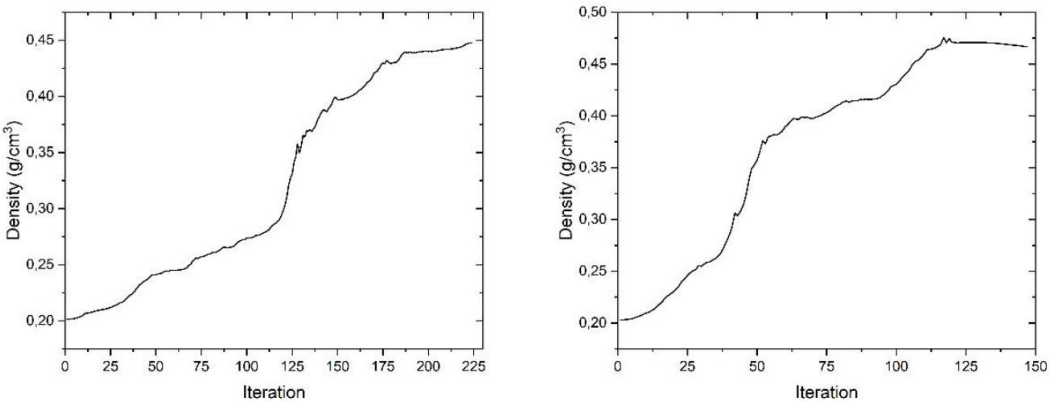
The unit cell volume change of pernigranil is shown in Fig.8. While convergence was achieved in 225 iterations to 1450 Ang^3 with unit cell volume change, convergence was achieved in 150 iterations in NO doping to 1380 Ang^3.



(a) (b)

Figure-8 Unit Cell Volume Change (a)4PANI PB-CO, (b) 4PANI PB-NO

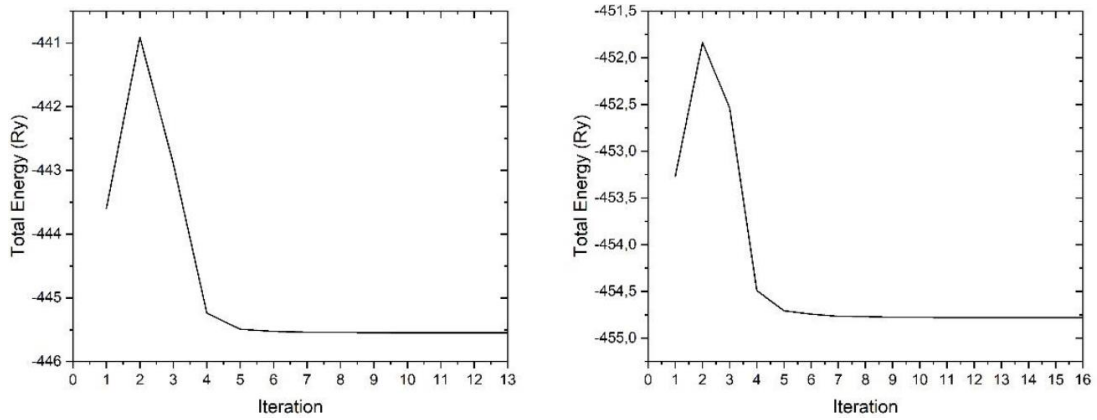
The unit cell density variation of 4 PANI PB-CO and 4 PANI PB-NO was obtained by the VC-Relax process as seen in Figure-9. Unit cell density for 4 PANI PB-NO has increased from 0.20 g/cm^3 to 0.45 g/cm^3 and from 0.20 g/cm^3 to 0.46 g/cm^3 for 4 PANI PB-CO.



(a) (b)

Figure-9 Unit Cell Density Change (a)4PANI PB-CO, (b) 4PANI PB-NO

The variation of 4 PANI PB-CO and 4 PANI PB-NO data obtained by SCF optimization in this study is presented in Figure-10. As can be seen from the graph in Fig.10(a), it has been determined that the total energy has changed exponentially since the second iteration and converged at the end of 13 iterations. In this case, the resulting energy Fermi level is 2.0175 eV. From the graph in Fig.10(b), it was determined that the total energy changed exponentially after the 3rd iteration and converged at the end of 15 iterations. In this case, the resulting energy Fermi level is -2.0175 eV.

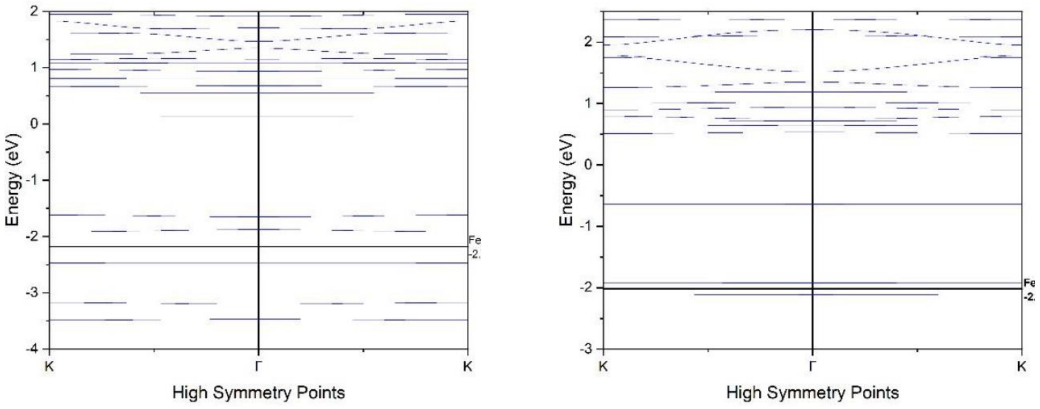


(a) (b)

Figure-10 Total Energy Optimizations with SCF Process (a) 4 PANI PB-CO, (b) 4 PANI PB-NO

After optimization with SCF process, 4PANI PB-CO and 4PANI PB-NO energy band gap calculations were made. The variation of the energy band values with high symmetry points and the energy Fermi level are shown in Fig.11. The E_{GAP} calculation is made from the difference between the lowest energy band (LUMO) above the Fermi energy and the highest energy band (HOMO) below the Fermi energy level. Accordingly, the data obtained are LUMO -2.4692 eV, HOMO -1.8768 eV, Fermi -2.1792 eV, band gap 0.5924 eV for 4 PANI PB-CO and LUMO -

2.1085 for 4 PANI PB-NO eV is HOMO -1.9263 eV, Fermi -2 is 0175 eV and the band gap is 0.1822 eV.



(a) (b)

Figure-11 Energy Band Values (a) 4 PANI PB-CO, (b) 4 PANI PB-NO

Results

By using TUBITAK TRUBA sources, conductivity properties of insulating pernigranilin material were investigated by doping with Quantum Espresso software.

When the literature is examined, it is seen that NH3 doping [6] or Cl doping [7] is made in polyaniline group materials. In this study, electrical conductivity changes of pernigranil as a result of doping of the insulator with CO and NO were determined. In other words, the semiconductor properties of the obtained pernigranil are in harmony with the studies in the literature.

It is assumed that there is a bandgap region called the “Fermi level” between the valence bond and conduction bond. The energy value of this region is higher than 1.5 eV for Fermi level or bandwidth. A higher energy is needed to transfer it to the conduction band [8]. It was stated that the band gap of the double-layer PANi selenium-tellude sheets was 1.4 eV [9].

Acknowledgement

The numerical calculations reported in this paper were fully/partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources).

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