

# Computational Study of Hydroxy Chalcone Compound as Potential Chemosensor for Cyanide Anion

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**Abstract** – A theoretical computational study has been carried out to study the interaction of hydroxy chalcone (COH) compound as chemosensors for  $CN^-$  anion. This research is modeling the molecular structure of hydroxy chalcone (COH) compound and its interaction model with  $CN^-$  using DFT method. The results of geometry optimization show an O-H bond lengthening of 0.7 Å with its interaction with the  $CN^-$ . This indicates the formation of a strong hydrogen bond causing deprotonation of the hydroxy chalcone (COH) sensor by the  $CN^-$ . The hydroxy chalcone (COH) sensor which is deprotonated has a large interaction energy that is -224.75 kJ/mol. Sensors that are deprotonated cause the HOMO-LUMO energy difference to decrease from -3.94 eV to -2.62eV.

**Keywords** – chemosensor, hydroxy chalcone, cyanide, DFT

## I. INTRODUCTION

Cyanide is an interesting anion because it is known to be highly reactive and is toxic to biological systems and the environment [1]. In very small amounts, cyanide can cause disorders of blood vessels, heart, vision, endocrine enzymes, central nervous and metabolic processes [2]. Cyanide can also inhibit the use of oxygen in cells and interfere with the activity of oxidasitochrome [3]. Cyanide can then be absorbed into the lungs, digestive tract and skin so that it can cause vomiting, seizures, loss of consciousness and even death [4]. Although toxic, cyanide is widely used in various processes and raw materials in synthetic fibers, synthetic resins, pesticides, medicines, fertilizer and gold and silver extraction processes [5]. According to the World Health Organization (WHO), the amount of cyanide allowed in drinking water is only 1.9 µM [6].

Various methods have been carried out to detect the presence of cyanide such as titration [7], chromatography [8], and electrochemistry [9]. But these

methods have drawbacks such as requiring a lot of analysis time, expensive costs, and often less sensitive and selective. Therefore, in the last few years chemosensor have been developed to detect cyanide anions. Chemosensor has many advantages such as high sensitivity, simple, fast results, and can be analyzed from the change in color given by the sensor compound [10].

One of compound that is believed to be a potential sensor compound is the chalcone compound. Structurally, chalcone compounds have two aromatic rings connected by a double bond  $C\alpha=C\beta$ . Chalcone compounds can be modified by adding substitution groups and one of them is a hydroxy (OH) group. The existence of this hydroxy group is expected to be the center of activity that will interact with cyanide [11]. Interactions between hydroxy groups and cyanide are expected to form hydrogen bonds [12].

Studies using computational chemistry calculations can be used to examine the interaction of sensor compounds and anions. One of the advantages of computational chemistry is that it can visualize the structure of sensor compounds and their interactions with anions [13]. One of the computational chemistry calculation methods that can be used in predicting the interaction of sensor and anion compounds is the density functional theory (DFT) method [14]. Calculations using the DFT method can give good results for calculations involving interactions such as hydrogen bonds or van der Waals [15].

In this research, a computational study regarding the potential of hydroxy chalcone compound (COH) as a cyanide anion sensor ( $CN^-$ ) was conducted. The results of this theoretical study are expected to provide comprehensive information in assisting the synthesis of

sensors of hydroxy chalone (**COH**) derivative compounds in the Laboratory.

## II. METHODS AND MATERIALS

### A. Materials of Study

The study materials used in this study were hydroxy chalone (**COH**) compounds as sensor molecules and cyanide anion ( $\text{CN}^-$ ) as target molecules. The structure of chalone derivatives as sensors and their interactions with anions is shown in Figure 1.

### B. Computational Calculations

All calculations are performed using Gaussian 09 software [16]. Prediction of the interaction model between the sensor compound (**COH**) and the cyanide anion ( $\text{CN}^-$ ) is done by optimizing the sensor complex geometry (**COH**)- $\text{CN}^-$  using the DFT 6-31G(d,p) method with the B3LYP density function. Next, the interaction energy of the sensor compound (**COH**) and  $\text{CN}^-$  anion is calculated by the same method. The absorption and transition energy properties of the sensor (**COH**) and sensor ion (**COH**) $^-$  calculated using the TD-B3LYP/6-31G(d,p) method. Observation of the effect of solvents on optical properties in the molecular system is carried out using DMSO and methanol solvents, calculated using a polarized continuous model (PCM) with the TD-DFT method [17]. Interaction energy ( $\Delta E_{\text{interaction}}$ ) is calculated from the difference between the sensor complex energy (**COH**)- $\text{CN}^-$  ( $E_{\text{COH}---\text{CN}^-}$ ) and total sensor energy (**COH**) and  $\text{CN}^-$  anion [18].



Figure 1. Structure of hydroxy chalone (**COH**)

## III. RESULTS AND DISCUSSION

The mechanism of sensor interaction (**COH**) and  $\text{CN}^-$  anions is analyzed by optimizing the geometry of the molecular complex (**COH**)- $\text{CN}^-$  using the *density functional theory* (DFT) method. Geometry optimization is done by making the phenol (OH) group as a binding subunit which is the active side and the center of the reaction. The results of the optimization of the sensor geometry (**COH**) and  $\text{CN}^-$  anion are shown in Figure 1 and Table 1.

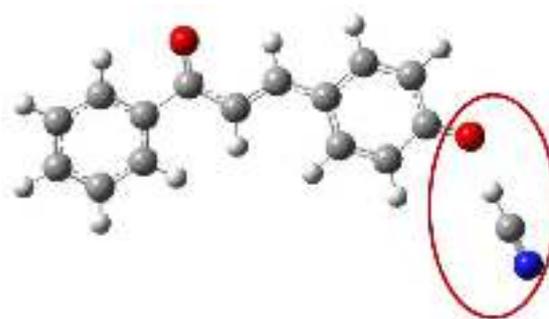


Figure 2. Geometry optimization of sensor interaction (**COH**) and  $\text{CN}^-$  anion

The length of the O-H bond on the sensor molecule after geometry optimization is 0.97 Å. After interaction with the  $\text{CN}^-$  anion, the O-H bond length became 1.67 Å. O-H elongation of 0.7 Å indicates a break in the O and H and the sensor is deprotonated [19]. Breaking the binding in the binding subunit sensor will cause the transfer of intermolecular protons (IPT) with  $\text{H}^+$  to be bound to the anion [20]. Deprotonation of sensor compounds by anions will give color changes when tested in the Laboratory [21]. In addition, optimization of the sensor molecular geometry (**COH**) and the  $\text{CN}^-$  anion results in a distance between O-H and  $\text{CN}^-$  which is smaller than 3 Å and the formation of angles formed between O-H and  $\text{CN}^-$  which is greater than 110°. This shows the occurrence of hydrogen bonds between O-H as a binding sensor unit with  $\text{CN}^-$  [22] [23].

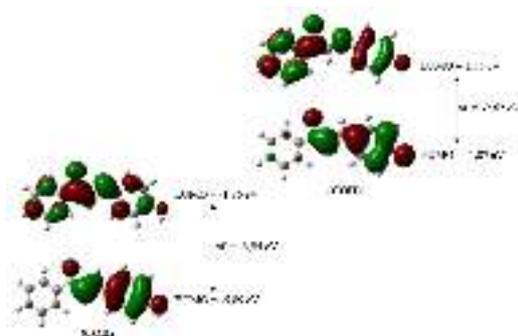
Table 1. Geometry sensor parameter (**COH**) and cyanide anion ( $\text{CN}^-$ )

Molecule	$r_{\text{(O-H)}} (\text{Å})$	$r_{\text{(H---CN}^-)} (\text{Å})$	$\theta_{\text{(O-H---CN}^-)} (^\circ)$
( <b>COH</b> )	0,97	-	-
( <b>COH</b> )--- $\text{CN}^-$	1,67	1,12	175,28

Table 2. Interaction energy (**COH**) and cyanide anion ( $\text{CN}^-$ )

Molecule	$-\Delta E_{\text{interaction}} (\text{kJ/mol})$
( <b>COH</b> )--- $\text{CN}^-$	224,75

The process of sensor deprotonation can also be analyzed from the sensor and anion interaction energy. If the sensor and anion interactions are strong to cause deprotonation, the sensor and anion interaction energy will be of great value. The interaction energy calculation results are shown in Table 2. Sensor interaction (**COH**) and  $\text{CN}^-$  anion have a big interaction energy so that it supports the prediction result of geometry optimization that indicates the  $\text{CN}^-$  anion causes the sensor to deprotonate.



**Figure 3.** The changes of HOMO-LUMO energy in sensor (COH) and ion sensor (COH)<sup>-</sup>

Deprotonation that causes intramolecular charge transfer (ICT) in sensor interactions (COH) and CN<sup>-</sup> anion can be demonstrated by electronic transitions using *Frontier Molecular Orbitals* (FMOs) analysis and changes in HOMO-LUMO energy. The electronic transition from HOMO to LUMO causes changes in the spread of electrons in the sensor structure (COH). The FMOs form the sensor (COH) in a neutral state and the ion shaped sensor (COH)<sup>-</sup> after deprotonation is shown in Figure 3. The electron  $\pi$  on the sensor (COH) in the neutral state comes from the double bond C=C on the benzene ring and the enon group C=O. Whereas in the ion-shaped sensor (COH)<sup>-</sup> after the transfer of intramolecular ICT charges, electrons  $\pi$  also originate from the lone pair of oxygen atoms in the O-H group. Electron pairs on oxygen which are negatively charged (COH)<sup>-</sup> can enter the ring due to resonance with double bonds. In the FMOs image (COH), it appears that electron density in HOMO is only distributed to the bound group and the enon group. The existence of electron excitation from HOMO to LUMO causes the flow of electrons in LUMO which is spread to all parts of the sensor (COH). Electron flow in sensor ions (COH)<sup>-</sup> greater than in neutral conditions. Electron scattering to all parts of the ion (COH)<sup>-</sup> indicates the transfer of intramolecular charge (ICT) to the sensor (COH) and anion interactions.

Changes in HOMO-LUMO energy in sensor (COH) and ions in the form of ions (COH)<sup>-</sup> which undergo intramolecular charge transfer (ICT) will also be related to the optical properties shown through the prediction of UV-Vis spectra. The prediction peak of UV-Vis spectra on the sensor ion (COH)<sup>-</sup> occurs at a larger wavelength. This proves that the small difference in HOMO-LUMO energy will cause UV-Vis adsorption to occur in larger wavelengths. In the electronic transition, prediction has been proven the difference in energy of the HOMO-LUMO sensor at ion condition (COH)<sup>-</sup> smaller than in the sensor (COH) neutral conditions. Table 3 shows the results of absorption of the UV-Vis sensor (COH) and ion sensor (COH)<sup>-</sup> which were calculated using the PCM TD-B3LYP/6-31G(d, p) method in DMSO and methanol solvents.

**Table 3.** Absorbed wavelength ( $\lambda_{\text{abs}}$ ), oscillator strength ( $f$ ) sensor (COH) and ion sensor (COH)<sup>-</sup> in DMSO and metanol solvents

Solvent	(COH)		(COH) <sup>-</sup>	
	$\lambda_{\text{abs}}$	$f$	$\lambda_{\text{abs}}$	$f$
DMSO	355,84	0,8253	436,52	0,9900
Methanol	353,99	0,8177	433,38	0,9619

#### IV. CONCLUSION

Computational studies conducted in this study provide a description of hydroxy chalcone compound (COH) as a potential chemical sensor of cyanide anion (CN<sup>-</sup>). The results of the analysis of sensor interactions (COH) with anion CN<sup>-</sup> indicate the formation of strong hydrogen bonds that cause sensor deprotonation (COH).

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