

<Research Paper>

Electrochemical Study for 1,3-Bisdicyanovinylindane

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Abstract: The electrochemical study has been enjoyed in many areas of chemistry. Through this approach using electrochemical measurement, empirical HOMO and LUMO values can be calculated by three methods such as absorption measurement, cyclic voltammetry and computational calculations. In this study, 1,3-bisdicyanovinylindane was prepared and investigated toward its optical properties. The absorption intensities were changed depending on changes of pH. These absorption changes are induced by resonance form of 1,3-bisdicyanovinylindane. The electron delocalization in π system is related to the resonance form. In accordance with this electron density distribution and HOMO/LUMO values of 1,3-bisdicyanovinylindane were simulated and calculated by *Material Studio 4.3*, absorption measurement and cyclic voltammograms. The 1,3-bisdicyanovinylindane is one of the most attracted acceptor units in D- π -A system. This attempt is useful to determine more detailed characteristics of the energy potentials.

Keywords: HOMO, LUMO, absorption, cyclic voltammetry, 1,3-bisdicyanovinylindane, D- π -A

1. Introduction

Donor(D)-acceptor(A) substituted organic molecules have been widely investigated due to their potential applications such as optical modulations, molecular switching optical memory and frequency doubling¹⁾. Among these molecules, 1,3-bisdicyanovinylindane is much used as the function of the electron's flowing through D- π -A system. This acceptor, namely malononitrile has been enjoyed as representative electron pulling strength and capacity within the molecular chromophores¹⁻³⁾.

In this D- π -A system, molecular properties can be affected by the types of donor and acceptor. In addition, the electron distributions and HOMO/LUMO energy potential values are important factors of molecular properties. This is associated with molecular orbital, identification of electron transitions^{4,5)}. In addition, functions of proton transfer or unshared pair/empty orbital interaction are also related⁶⁾. In this regard, the electrochemical study of molecules to investigate electron density distributions and HOMO/

LUMO energy potential values are noteworthy. There are three methods of experimental approaches for this investigation. Absorption measurement, cyclic voltammetry and computational calculations are involved.

In this work, 1,3-bisdicyanovinylindane, widely used indicator dye in D- π -A system, was studied for its optical properties in accordance with different pH conditions and HOMO and LUMO energy levels. Energy potential values of onset and peak values from oxidation peak were determined by absorption measurement and cyclic voltammetric measurement, respectively. In addition, computational calculations for the energy potential values and electron density distributions were also simulated by the simulation module named *Material Studio 4.3 package program*.

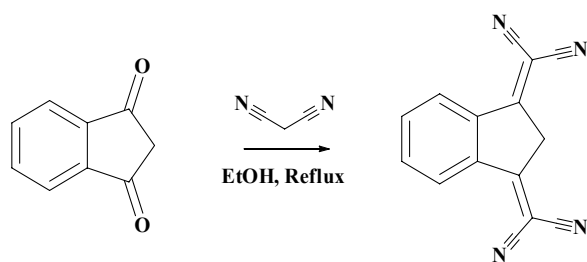
2. Experimental

2.1 1,3-Bisdicyanovinylindane (BDV)

1,3-Bisdicyanovinylindane (BDV) was synthesized through the reaction of 1,3-indanedione and malononitrile as shown in the scheme 1. BDV was prepared according to literature method⁷⁻⁹⁾. Mixture of 1,3-indanedione (14.9mmol, 2.18g) and malononitrile (44.7mmol,

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2.95g) in ethanol (50ml) was prepared and stirred at room temperature for 15 min and sodium acetate (3.05g) was then added. The reaction mixture was refluxed for 3h. After reaction was complete, mixture was allowed to cool to room temperature. The blue solution was then filtered to remove monocondensation product such as 3-dicyanovinylindan-1-one. The filtrates were diluted with water (100ml) and acidified using hydrochloric acid to give a white solid precipitate. The precipitate was filtered off, washed thoroughly and dried⁸⁾. Yield: 55.59% (2.01g); calculated for C₁₅H₆N₄: C, 74.37; H, 2.50; N, 23.13. Found: C, 74.78; H, 2.49; N, 23.48; m/z (M⁺): 242⁸⁾.



Scheme 1. The synthetic method for BDV.

2.2 Measurements

The spectroscopic characteristics were examined and determined using *Agilent 8453* UV-Vis spectrophotometer. The electro-chemistry properties of these dyes were examined with a *Versa STAT 3* using a platinum wire served as a working electrode, and Ag/Ag⁺ electrode served as a reference electrode and a carbon served as a counter electrode. The scan rate was 50mV/s. The optimized geometry structure and molecular energy potentials were calculated with *Materials Studio 4.3*.

3. Results and Discussion

In our previous work^{7,9)}, this BDV was studied for pH indicator materials. In this regard, the prepared BDV was firstly investigated for absorption changes depending on different pH conditions with UV-Vis absorption spectrometer. To control pH conditions of BDV solution, hydrochloric acid and sodium hydroxide were used.

As shown in Figure 1, absorption band centered at 584nm appeared with showing weak intensity in acidic condition. On the other hand, absorption intensity was dramatically enhanced by changing of pH conditions from acid to alkali. This result indicated that BDV can change its own color strength depending on pH conditions. This phenomenon is related to the resonance effect in the BDV structure^{7,8)}. In acidic condition, BDV was reacted with proton and was shown with weak color. In contrast, the alkali condition makes a reaction for isolation and dissociation between BDV and proton. The absorption intensity was increased by showing a deep color change. The probable mechanism of resonance form for BDV was depicted in Scheme 2.

The resonance form of BDV must be occurred by electron delocalization in π system⁸⁾. In this regard, HOMO/LUMO energy potential values and electron density distributions can be one of the important considerations to approach its molecular own properties.

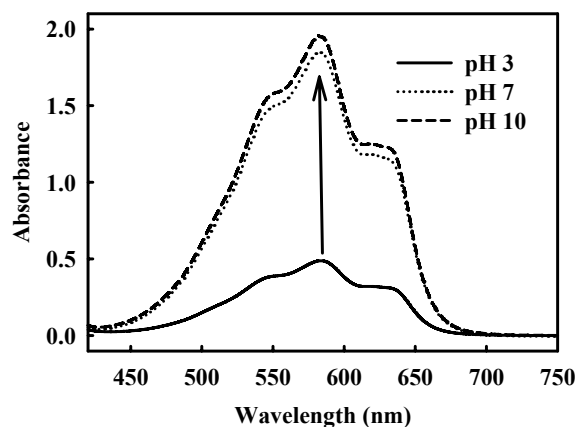
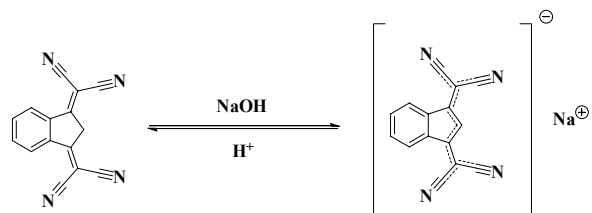


Figure 1. UV-Vis spectra of DYE 1 (100µM) depending on different pH conditions.



Scheme 2. The probable mechanism of resonance form for DYE 1 depending on pH conditions^{7,8)}.

According to this context, absorption measurement, cyclicvoltammogram and computational calculation were carried out using BDV.

At first, the band-gap energy of BDV was determined by using absorption measurement. In Figure 2, absorption edge was obtained for 661nm, indicating the λ value in following equation (1)^{6,10,11}. The band-gap energy of BDV was calculated and determined as 1.876eV.

$$eV = 1240 / \lambda \text{ from absorption edge} \dots\dots\dots (1)$$

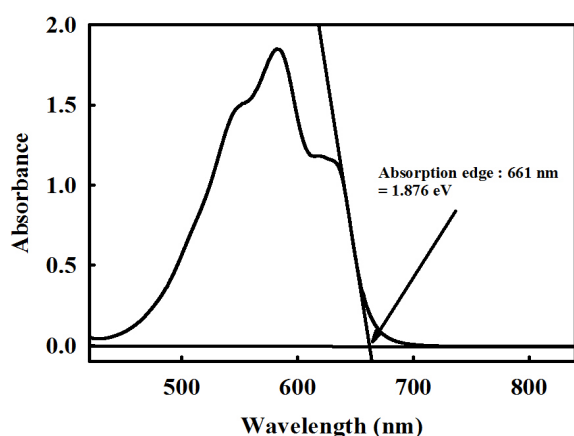


Figure 2. UV-Vis band-gap measurement of BDV (100 μ M).

Furthermore, cyclicvoltammogram was also studied to obtain HOMO and LUMO values. These values can be calculated from the peak and the onset potential values with cyclicvoltammogram as shown in Figure 3. The oxidation peak was definitely observed in this spectrum. Thus, HOMO potential energy values were calculated with the following equation (2). $E_{1/2}$ (Ferrocene) values of 0.42V were applied in this equation^{6,10,11}.

$$HOMO (eV) = -4.8 - (E_{\text{peak/onset}} - E_{1/2} \text{ (Ferrocene)}) \dots\dots\dots (2)$$

Through this equation (2), each HOMO value was obtained for -5.28eV and -4.58eV, respectively.

These values were calculated from the peak and the onset values. LUMO value was also determined by using the above results of band-gap energy for absorption measurement and HOMO values for

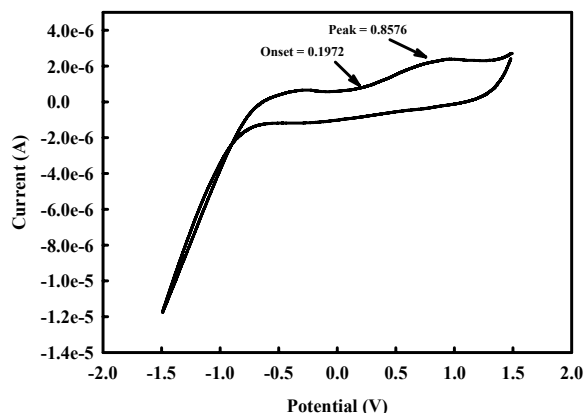


Figure 3. Cyclicvoltammogram of BDV (100 μ M) in MeCN. Tetrabutylammonium perchlorate was added for electrolyte.

cyclicvoltammogram. -3.36eV and -2.70eV were calculated for the corresponding peak and onset potential values.

Finally, electron density distributions and energy potential values for HOMO and LUMO states were simulated and calculated by *Material Studio 4.3*, the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof function of generalized gradient approximation level with double numeric polarization bases set was used to calculate the energy level of the frontier molecular orbitals¹²⁻¹⁴. The result was described in Figure 4.

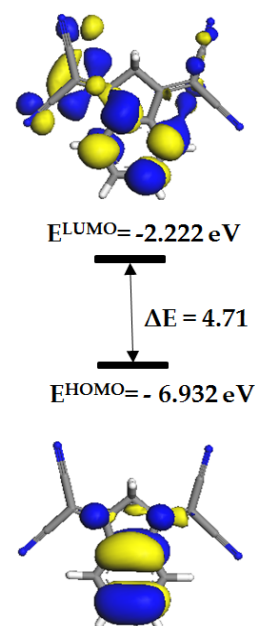


Figure 4. HOMO/LUMO energy levels and electron density distributions for BDV.

Table 1. HOMO/LUMO and band-gap energy potential

Type	Onset (eV)			Peak (eV)			Computational Calculation (eV)		
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
BDV	-4.58	-2.70	1.88	-5.24	-3.36	1.88	-6.93	-2.22	4.71

Electron density distribution of BDV from HOMO was mainly located on indanedion part. On the other hand, significant changes of electron density appeared in dicyanide part showing the electron density in the only LUMO state. The redistribution of electron density for HOMO and LUMO is related to the interaction of dye molecule with its environmental conditions¹⁵⁾. The energy potential values of HOMO and LUMO were also monitored for -6.932eV and -2.222eV, respectively.

All results of HOMO and LUMO values and band-gap energy potentials for BDV were arranged and compared in Table 1. Band-gap energy potential values showed much difference between absorption measurement and computational calculation. However, HOMO and LUMO values relatively showed a little difference. In addition, only LUMO values obtained from absorption measurement and cyclicvoltammogram were similar to computational calculated LUMO value.

4. Conclusions

In this study, 1,3-bisdicyanovinylindane (BDV) was synthesized and investigated for its optical properties and energy potential values. In optical properties, absorption was changed with depending on different pH values. In alkali condition, the absorption intensity showed the strongest value compared with other two pH conditions such as neutral and acid. This is related to the resonance effect of BDV induced by the reaction with protons. HOMO, LUMO and band-gap energy values were also investigated by absorption measurement, cyclicvoltammetry and computational calculation.

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