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1.10-Phenanthroline as Anti-Radiation UV Agent: Spectrophotometry Analysis and Modeling

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I. Introduction

The 1.10-Phenanthroline (Fig. 1)is one ofthe organic compounds which are soluble in water and organic solvents such as alcohol and acetone [1,2,3]. 1.10-Phenanthroline is the white crystalline powder that has a melting point of 93-94 °C with a molecular weight of 180.20 grams/mol. The structure of the compound 1.10-phenanthroline (C12H8N2) consists of 3 benzene rings with two nitrogen atoms which have a quiet electron pair in the compound [5,6,7].

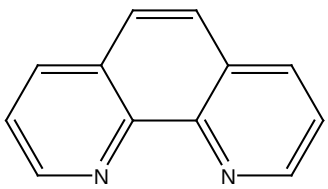

Figure 1: Molecule of 1.10-phenanthroline

1.10-phenanthroline compounds are often used as ligands that are used as catalysts, complexation of transition metal ions and various biological activities [8-11].Research on 1.10-phenanthroline compounds has been carried out such as spectroscopic characterization, molecular structure studies, anti-cancer / tumor, anti-microbial and so on [12-17]. 1.10-Phenanthroline includes derivatives of aromatic compounds (3 benzene) with conjugated bonds [18, 19]. Aromatic compounds have the potential as anti-UV radiation, where aromatic derivatives such as chalcone and anthocyanin show good results as anti-UV agents in UV-B (290-320 nm) and UV-A (320-375 nm) [20, 21]. This article reports the activity of 1.10-phenanthroline as an anti UV agent and an electronic transition model using the ZINDO/s semi-empirical method.

II. Methodology

a) Measurement of Pigmentation Percent (% Tp), Percent Erythema (% Te) and SPF

Percent pigmentation measurements, percent erythema, and SPF were carried out in wavelength ranges of 290-375 nm with 5 nm intervals using variations in concentrations of 0.1, 0.5, 1, 5 and 10 ppm. Percent pigmentation (% Tp), percent erythema (% Te) and SPF can be determined based on the absorbance value of the UV-Vis spectrophotometer. [22, 23].Determination of AUC Area Value (Area under Curve) is determined based on the absorbance value of each wavelength and SPF (Sun Protection Factor) value determined in each concentration variant.

b) 1.10-Phenanthroline Molecular Geometry Modeling

Optimization of 1.10-Phenanthroline molecular geometry aims to find the optimal molecular structure with the smallest energy value [24]. Modeling molecular geometry and molecular energy calculations can be determined using the semi-empirical method of PM3 [25]. Optimization of 1.10-Phenanthroline molecular geometry uses the semi-empirical method PM3 with a gradient limit of change of 0.001 kcal/(Å.mol) reaching the near gradient limit based on the Polak-Ribiere method.

c) Electronic Transition Studies

Modeling the structure of geometry optimization results from the semi-empirical method of PM3, followed by the semi-empirical method of ZINDO / s to produce electronic transition spectra data. The transition calculation criteria use single point configuration interaction (CI) calculations with a singly excited-CI excitation limit with HOMO-LUMO orbitals respectively 2. The electronic transition of 1.10-phenanthroline was analyzed from a discontinuous spectral diagram of the modeling results.

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III. Results And Discussion

a) Potential 1.10-Phenanthroline as an Anti-Radiation Agent for UV

The measurement of the absorbance value at 1.10-Phenanthroline shows that there is a decrease in the consecutive absorbance of the UV-B wavelength to UV-A (Figures 2 and 3). The higher absorbance value of UV-B of 1.10-phenanthroline compounds showed that UV-B deterrent activity was better than UV-A. The potential of the 1.10-Phenanthroline compound as an anti-UV radiation agent was reviewed based on percent pigmentation (% Tp), percent erythema (% Te) and SPF values.

The measurement results of absorbance of 1.10-phenanthroline compounds in the UV-B wavelength range (290-320 nm) showed that the optimum concentration was at a concentration of 10 ppm with an absorbance value of 0.512 precisely at a wavelength of 290 nm. Whereas, the results of absorbance measurements at UV-A wavelength (325-375 nm) showed that the optimum concentration was at a concentration of 10 ppm with an absorbance value of 0.074 at a wavelength of 325 nm.

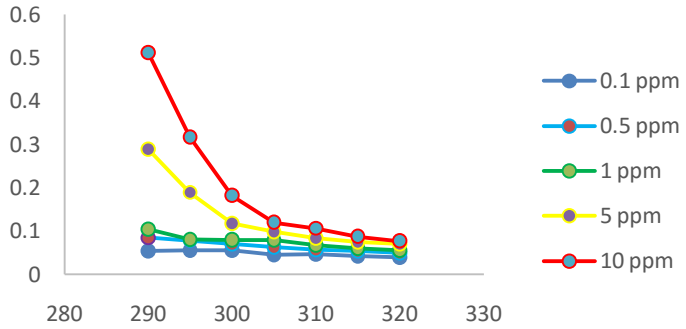


Figure 2: Absorption Graph of 1.10-Phenanthroline in the UV-B Area

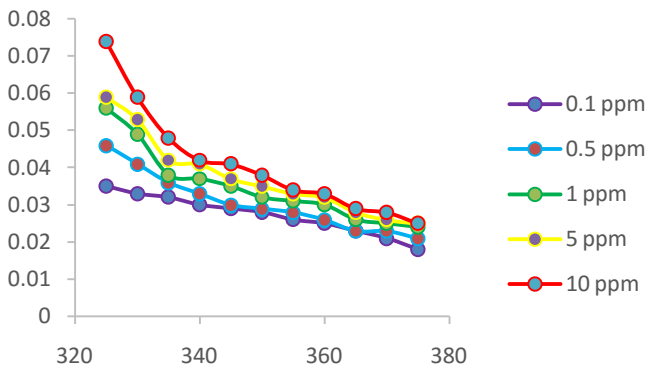


Figure 3: Absorption Graph of 1.10-Phenanthroline in the UV-A Area

The resulting test of thepercent of erythema (% Te) and SPF of compound 1.10-Phenanthroline was carried out in the UV-B area with the results showed that the% Te value with the lowest value was at a concentration of 0.1 ppm and the highest SPF was at a concentration of 10 ppm (Table 1). The lower of erythema shows good potential as anti-UV, where the average %Te shows the sunblock protection category. The greater the SPF shows good ability as an anti-UV agent [26], and the optimum SPF at 10 ppm 1.10-Phenanthroline shows a minimum UV protection category.

Table 1: Percent of Erythema and SPF 1.10-Phenanthroline

C (ppm)	absorbance							%Te	SPF
	290	295	300	305	310	315	320		
0.1	0.054	0.056	0.056	0.045	0.047	0.042	0.039	0.102	1.265
0.5	0.085	0.078	0.07	0.063	0.057	0.053	0.049	0.134	1.364
1	0.104	0.081	0.08	0.079	0.068	0.061	0.056	0.156	1.431
5	0.289	0.189	0.117	0.098	0.083	0.074	0.07	0.245	1.759
10	0.512	0.317	0.182	0.12	0.106	0.088	0.077	0.367	2.328

The percentage of pigmentation (%Te) was measured at the wavelength of the UV-A area, where the lower %Te showed better anti-UV activity. The results of the percent pinging test showed that the lowest%Tp value was at a concentration of 0.1 ppm (Table 2). The average yield of 1.10-Phenanthroline compound pigmentation value based on concentration variants shows the sunblock category. The greater %Te and %Tp in skin care products can cause skin irritation. [27].

Table 2: Percent of Pigmentation of 1.10-Phenanthroline

C (ppm)	absorbance											%Tp
	325	330	335	340	345	350	355	360	365	370	375	
0.1	0.035	0.033	0.032	0.03	0.029	0.028	0.026	0.025	0.023	0.021	0.018	0.509
0.5	0.046	0.041	0.036	0.033	0.03	0.029	0.028	0.026	0.023	0.023	0.021	0.514
1	0.056	0.049	0.038	0.037	0.035	0.032	0.031	0.03	0.026	0.025	0.024	0.520
5	0.059	0.053	0.042	0.041	0.037	0.035	0.033	0.032	0.028	0.026	0.025	0.525
10	0.074	0.059	0.048	0.042	0.041	0.038	0.034	0.033	0.029	0.028	0.025	0.532

b) Geometry Optimization and Electronic Transition

Optimization of 1.10-Phenanthroline molecular geometry was carried out using the semi-empirical PM3 method found in the *Hyperchem* 8.0.10 application [28]. One parameter for predicting a structure that has the optimum geometry is to have the smallest total energy which is the total amount of binding energy, and heat of formation. The geometry optimization results of the 1.10-Phenanthroline molecule involved 22 atoms, and 66 electrons with measurement parameters including total energy, binding energy, and formation heat (Table 3).

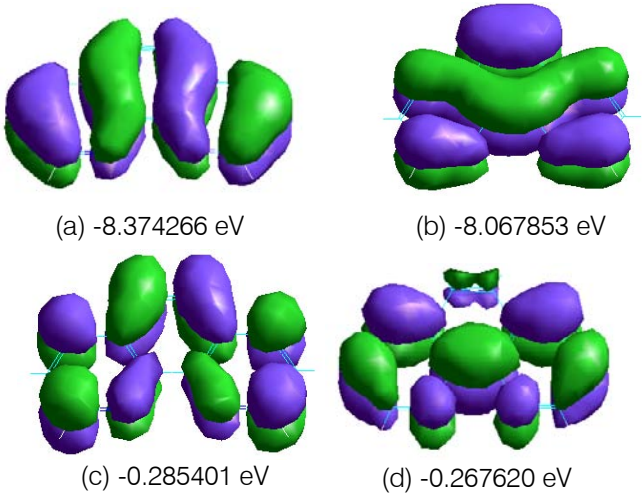
Table 3: Geometry Optimization of 1.10-Phenanthroline Using the PM3 Method

No.	Parameter	value
1.	Energy Total (kcal/mol)	-43084.3805
2.	Binding Energy (kcal/mol)	-2622.1956
3.	Heat Formation (kcal/mol)	71.3004

The electronic transition study was carried out using the ZINDO/s semi-empirical method by looking at the transition spectrum modeling [29]. Where the data were taken in the form of nm wavelength, oscillator strength, molecular orbital (MO) level, HOMO energy and LUMO energy to study the transition type of compound 1.10-Phenanthroline. Based on table 5 data obtained three peak wavelengths with oscillator strength values are in the UV region (Table 4). These results show the ability of 1.10-Phenanthroline compound through the simulation of ZINDO/s semi-empirical modeling with the optimum wavelength value at 250.50 nm. Also, the transition type at each peak in compound 1.10-Phenanthroline shows the transition type, namely n to π^* and π to π^*. Electronic transition activity at 1.10-Phenanthroline, when exposed to UV light, is affected by the π conjugated bond in the aromatic ring and the lone pair electron in the Nitrogen atom.

Table 4: ZINDO/s Method Simulation of 1.10-Phenanthroline

λ (nm)	Osc.	MO level	ΔE_g (eV)	Transition Judgments
278.9	0.0617	33→34 32→35	7.78 8.10	n→π*
250.5	1.8804	33→34 32→35	7.78 8.10	π→π*
234.7	0.9577	33→35 32→34	7.80 8.08	π→π*



(a) -8.374266 eV (b) -8.067853 eV

(c) -0.285401 eV (d) -0.267620 eV

Figure 4: MO level of complex 1.10-Phenanthroline (a), (b) HOMO 32, 33 and (c), (d) LUMO 34, 35

Electronic transition modeling using semi-empirical methods involves 64 molecular orbitals with different MO levels. The molecular orbitals(MO) levels involved in the electron excitation process are MO 32 (HOMO-1), 33 (HOMO), 34 (LUMO) and 35 (LUMO +1). The reactivity of a compound to UV light can be seen from the difference in HOMO to LUMO energy in the excitation of electrons [30, 31]. The electron excitation at MO 33 to 34 has the smallest energy difference, and MO 32 to 35 has the greatest energy difference of HOMO-LUMO (ΔEg) at the 1.10-Phenanthroline compound.

IV. Conclusion

The results of the activity of the 1.10-Phenanthroline compound as an anti-UV radiation agent showed that the highest absorption was in the UV-B wavelength region precisely at a concentration of 10 ppm of 0.512The highest SPF is 2,328 at a concentration of 10 ppm. The lowest%Te value obtained was 0.102% and the lowest %Tp obtained was 0.509%. The results of the 1.10-Phenanthroline molecular geometry optimization using PM3 semi-empirical method get an optimal structure with a total energy of -43084 (kcal/mol). Electronic transition modeling using the ZINDO/s semi-empirical method shows that there are three peaks with peak height at a wavelength of 250.50 nm (1.8804) and involving four molecular orbitals, namely HOMO (32.33) and LUMO (34.35). The type of transition found in 3 peaks in compound 1.10-Phenanthroline shows the transition types n to π^* and π to π^*.

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