

Photostabilization, Thermodynamic and Theoretical Studies of polystyrene by some 2-amino pyridine

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Abstract

Polystyrene (PS) films are photostabilized by 2-amino pyridine derivative compounds. Investigations were conducted on compounds of (a-e). The casting method was used to create PS films with complexes present in concentrations of 0.5 % by weight, while chloroform served as the solvent. By keeping track of the carbonyl indices as the exposure duration progressed, the photostabilization activities of these compounds were discovered. Using chloroform as a solvent, the variations in PS's viscosity average molecular weight with exposure time were also monitored. The theoretical results of the PS modification compounds showed that the total energy values of PS-D are higher energy content than the rest of the studied models. The negative sign in the HOMO energy indicates stability, that is, it is less effective, where values are shown (HOMO) PS-C is the least effective (stable) and PS-E is the most effective (unstable). The thermodynamic theoretical outcome was shown that all reactions are endothermic and spontaneous, and the results of the (energy gap) values gave a range from 2.38453 eV for PS-C to 2.60277 eV. For PVC-E, which proves that all PS modifications are conductive or semiconducting materials for electricity.

Keywords: 2-amino pyridine, Photochemistry, PS, Photostabilizer, FT-IR, Uv-light

Introduction

One of the most extensively used plastics is polystyrene, which is produced at a rate of several million tonnes annually. Although polystyrene is translucent by nature, colorants can be used to tint it. Protective packaging (like packing peanuts and in the jewel, cases used to store optical discs like CDs and occasionally DVDs), containers, lids, bottles, trays, tumblers, disposable cutlery, model-making, and as a substitute for phonograph records are just a few uses for this material [1]. During processing, a lot of polymers experience heat oxidative degradation. At room temperature, polymers can deteriorate over longer periods of time by autooxidation and photooxidation. The energy of this light is sufficient to start a photochemical process that results in material degradation in outdoor applications where the materials are exposed to UV sun radiation. Antioxidants, light, and heat stabilizers are frequently used to prevent plastics from this type of degeneration [2]. Due to their use in numerous fields, 2-aminopyridine compounds have long been recognized as a family of chemicals and continue to be intriguingly significant. 2-Aminopyridine is primarily used as an intermediary in the production of piroxicam and other medicines. New non-steroidal anti-inflammatory medicines of the oxicam class, such as lornoxicam and tenoxicam, are thought to work by blocking cyclooxygenase, a crucial enzyme for prostaglandin formation at the site of inflammation [3-5]. Mono Schiff base's photostabilizing impact on PS film has been researched [6-8]. To the best of our knowledge, there has never been an attempt to research how 2-aminopyridine compounds with Schiff bases can photostabilize PS films.

Experimental

Materials

The following 2-amino-4-(4-substituted-phenyl)-6-(4-((E)-(4-hydroxy-3-((E)-(2-oxoquinolin-1(2H-ylimino)methyl)phenyl)diazanyl)phenyl)nicotinonitrile (a-e) compounds were all prepared by the method previously described by Hameed [9] (**Figure 1**).

Films preparation

The ideal PS solvent is chloroform. By using an evaporation approach at room temperature for 24 hours, polymer films with a 40-micrometer thickness were prepared using fixed concentrations of PS solutions (5 %) in chloroform. Starting with a zero concentration (blank), the synthesized chemical compounds (2-amino pyridine derivatives) were applied to the films at a 0.5 % concentration by weight. The films were made using an evaporation procedure at room temperature for 24 h in order to get rid of any potential leftover solvent (chloroform). Film samples were then dried for a further 3 h at ambient temperature and low pressure. The films were mounted on a pedestal made specifically for irradiation (for 300 h), which was supplied by the Q-panel firm and is made of aluminum plate with a thickness of 0.6 mm [10].

Accelerated testing technique

A UV Light ($\lambda_{\max} = 313$ nm and light intensity = $6.2 \times 10^{-9} \text{ ein}^{-3} \cdot \text{dm} \cdot \text{s}^{-1} \text{ nm}$) was used to irradiation the PS films using an accelerated weatherometer QUV tester (Philips, Saarbrücken, Germany) at room temperature. To guarantee that the incident light intensity was the same on all sides, the PS films were occasionally rotated.

Rate of PS photodegradation (kd)

Using FTIR spectroscopy

The photodegradation of PS films was observed using the FTIR 4200 JASCO spectrophotometer (4000 - 400 cm^{-1}). Polymeric materials undergo changes in their chemical, mechanical, and physical properties when exposed to ultraviolet radiation. Carbonyl is produced as a result of photo-oxidation of PS. As a result, the variations in the carbonyl group's IR absorption bands (1726 cm^{-1}) were observed and compared to a reference peak (1328 cm^{-1}). Eq. (1) from the band index approach was used to obtain the indices for the carbonyl ($\text{I}_{\text{C=O}}$) group (50, 100, 150, 200, 250) h. Both the absorbance of the peak being studied (A_s) and that of the reference peak (A_r) are necessary for calculating the functional group index (I_s) [11].

$$I_s = A_s / A_r \quad (1)$$

By losing weight

Using Eq. (2), the weight of the polystyrene sample was converted into the percentage of weight loss during the irradiation process, where (W_1) represents the weight prior to irradiation and (W_2) represents the weight following irradiation.

$$\text{Weight loss\%} = [(W_1 - W_2) / W_1] \times 100 \quad (2)$$

The calculation method

The Gaussian 16, version D.01 software and the combination of Becke's 3-parameter hybrid (B3) exchange functional and the Lee-Yang-Parr (LYP) correlation functional (B3LYP) were used for all theoretical calculations of the chemicals included in the study. All geometry optimizations and frequencies the highest occupied molecular orbital energies (E_{HOMO}), and the lowest unoccupied molecular orbital energies (E_{LUMO}) are computed using a variation of the density functional theory (DFT) method using the basis set unrestricted 6-31G [12]. Help to evaluate other significant functions, such as ΔE , η , σ , and χ using Eqs. (3) - (8) see **Table 2**.

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3)$$

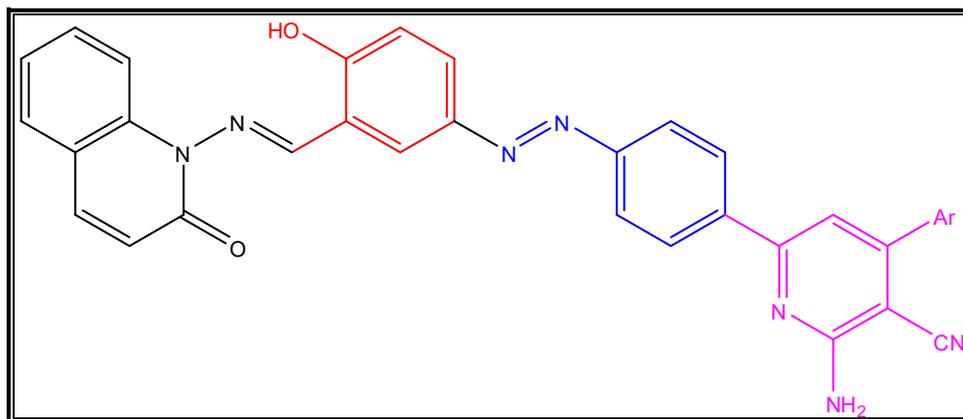
$$\eta = -\frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\chi = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (6)$$

$$I = -E_{\text{HOMO}} \quad (7)$$

$$A = -E_{\text{LUMO}} \quad (8)$$



Comp. No.	Ar.
a	
b	
c	
d	
e	

Figure 1 2-amino pyridine derivative compounds.

Results and discussion

FT-IR Spectra of PS Films

Compounds with 2-amino pyridine derivatives have been employed as PS film photostabilization additives. Changes in the infrared spectra of these compounds as a function of irradiation time at 313 nm were observed to evaluate the efficacy of these additions for the photostabilization of PS films.[13]

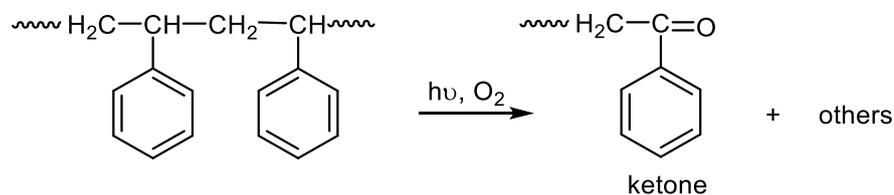


Figure 2 Formation of carbonyl fragment from photooxidative degradation of PS.

The PS (blank) films' FT-IR spectra were obtained both before and after irradiation, and the carbonyl group's intensity (1726 cm^{-1}) was contrasted with the reference peak's (1328 cm^{-1}) peak, which stands for the C-C bonds present in the polymeric chains of PS [10]. As seen in **Figure 3**, the intensity of the C=O group was much higher after radiation than before radiation.

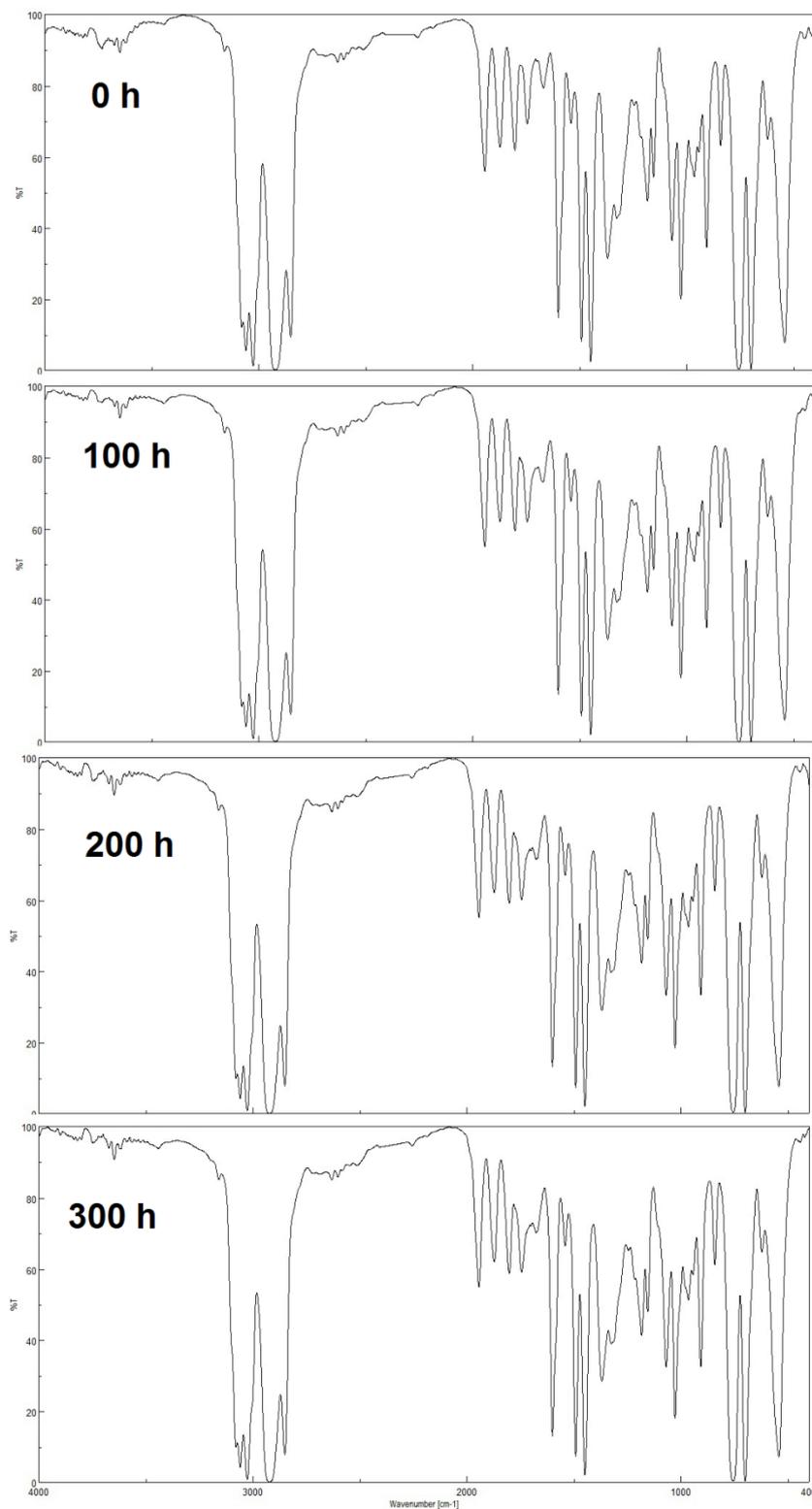


Figure 3 Change in the PS FT-IR spectra of the irradiated films for 300 h.

The FT-IR spectra were obtained every 50 hours when the PS films were exposed to radiation for up to 300 h. When compared to the results for the PS films containing pyridine derivatives a-e, the variations in the carbonyl intensity for the blank PS were considerable. These findings demonstrate the importance of the 2-aminopyridine derivatives a-e in stabilizing PS polymeric structures (**Figure 4**).

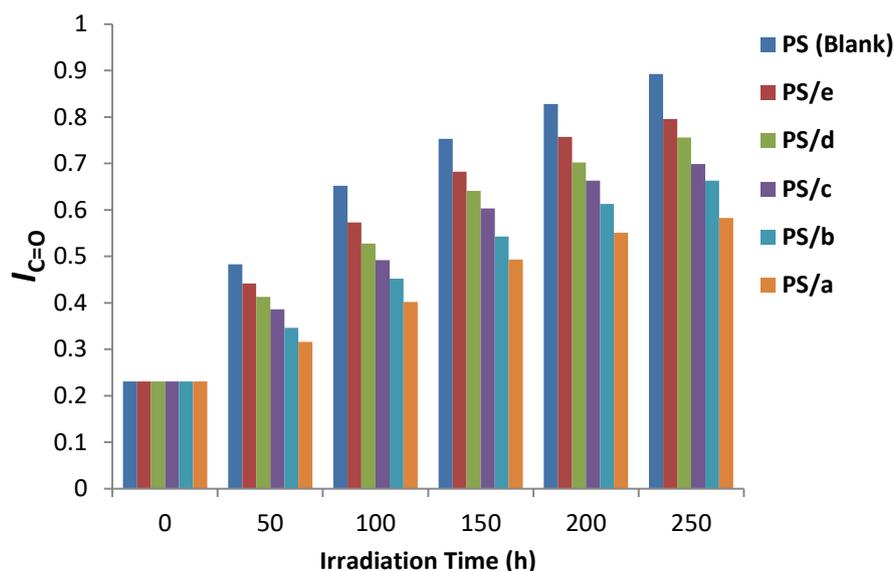


Figure 4 The PS carbonyl group index changed ($I_{C=O}$).

Weight loss of PS films

When PS is exposed to radiation, it undergoes a number of physical and chemical changes, including a change in hue and the production of different small-molecular-weight fragments. Long-term UV light exposure to PS causes it to lose weight as a result [10]. The amount of PS photodegradation can be determined by looking at the weight loss percentage. Based on previous studies using pyridine derivatives as a photoinhibition [14], a-e compounds were utilized at a low concentration of 0.5 % by weight of the 2-aminopyridine derivatives in PS films that contained 5 2-aminopyridine derivatives (0.5 wt%). The weight loss (%) was then calculated. Additionally, such a low concentration ensures that the additives are compatible with one another and prevents the coloring of polymeric films. The weight loss (%) attained as a result of irradiating polymeric films is shown in **Figure 5**. It was evident that using 2-aminopyridine derivatives caused the PS films to lose weight compared to the situation where no additives were applied. The strongest photostabilizing impact was demonstrated by a derivative of 2-aminopyridine, followed by others. The damaging irradiation (313 nm) that could disrupt or destroy the PS polymeric chains was apparently absorbed by pyridine derivatives [15,16]. Therefore, to increase the PS films' photostability, 2-aminopyridine derivatives a-e could be utilized as effective photostabilizers.

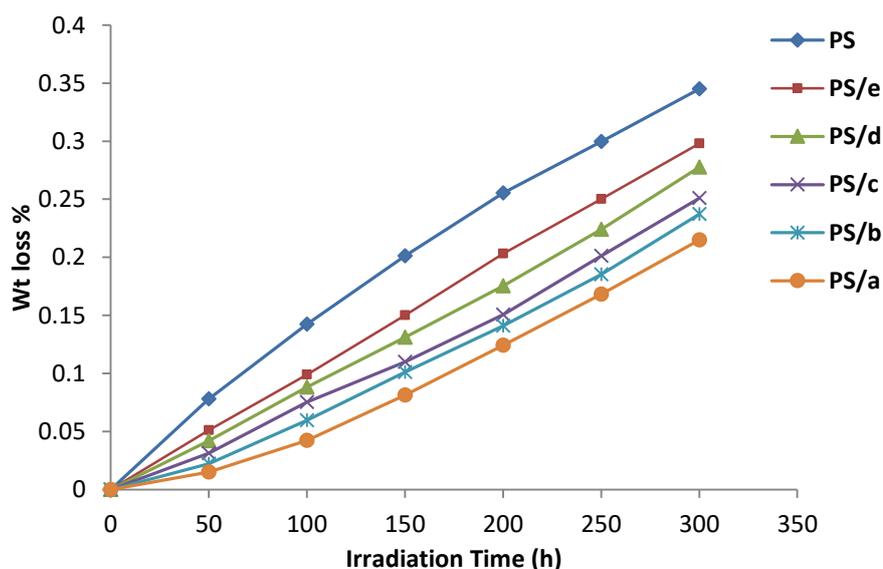


Figure 5 Change in the PS weight upon irradiation.

PS film optical microscopy

The findings proved that adding 2-aminopyridine derivatives a-e can slow down PS film photodegradation. Observing the potential effects of irradiation on the polymeric surface was intriguing. Accordingly, an optical microscope with 400× magnification was used to examine the surface morphology of the PS films before exposure to radiation (**Figure 6**).

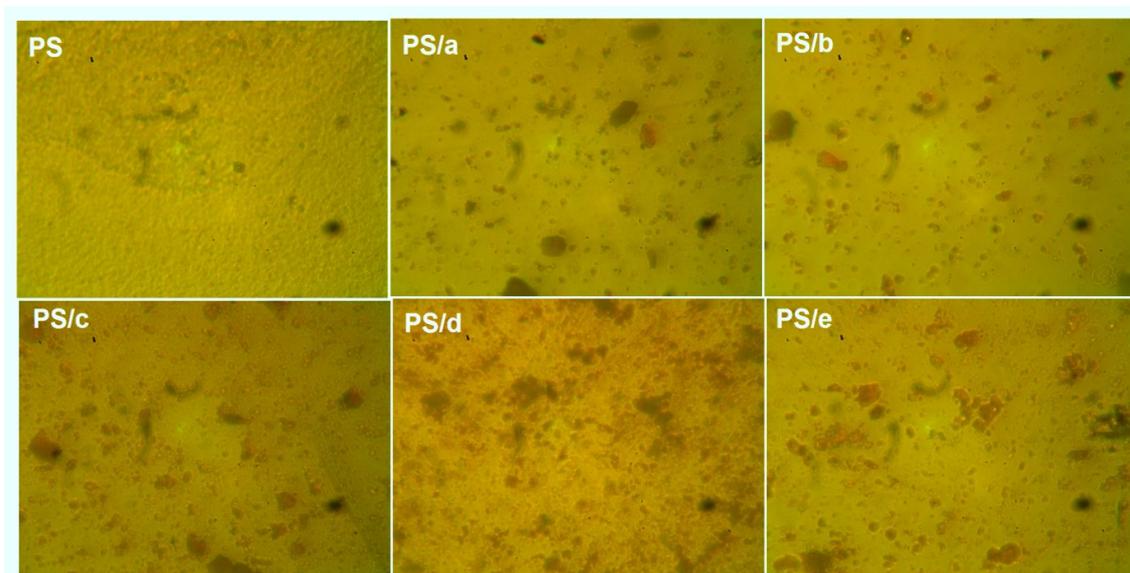


Figure 6 Optical images (400× magnifications) of the PS films before irradiation.

After exposure to radiation, the optical images of the PS films (**Figure 7**) revealed considerable discoloration, the production of pigment particles, cracks, grooves, and white spots in addition to rough surfaces. In the instance of the blank PS film, the adjustments had an impact. In contrast, the 2-aminopyridine derivative-containing PS films that were not irradiated showed fewer flaws. These findings demonstrate the effectiveness of pyridine derivatives as additives to improve PS film photostabilization under irradiation.

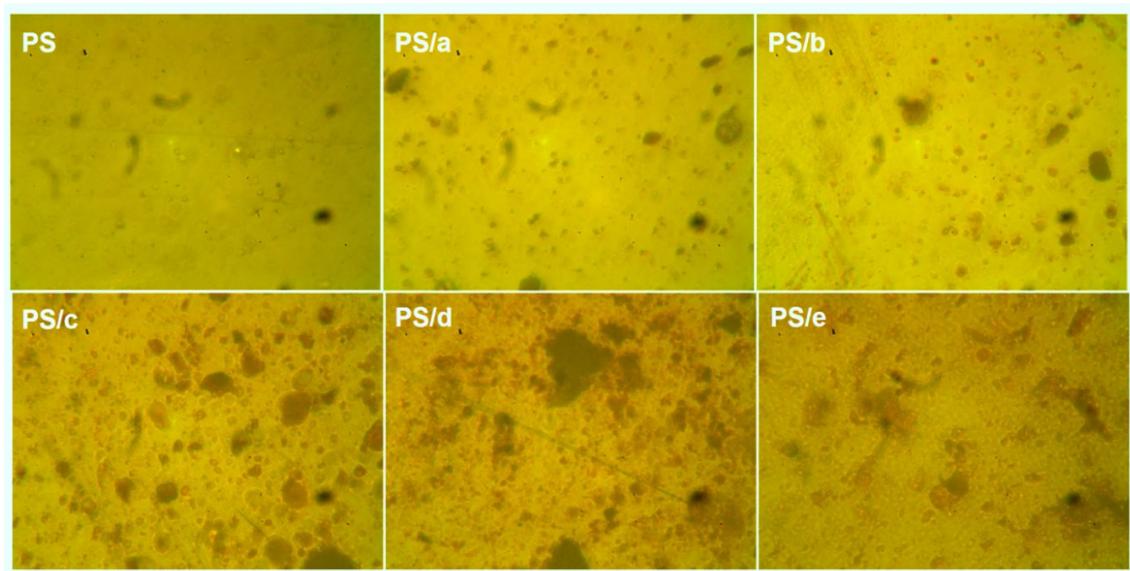


Figure 7 Optical pictures of the PS films following irradiation at 400× magnification.

Photostabilization mechanism of PS films

2-aminoPyridine derivatives are highly aromatics and therefore, they can act as UV absorbers [10]. The photo-oxidation of polystyrene leads to the formation of polymeric radical within the polymeric backbone (Figure 8).

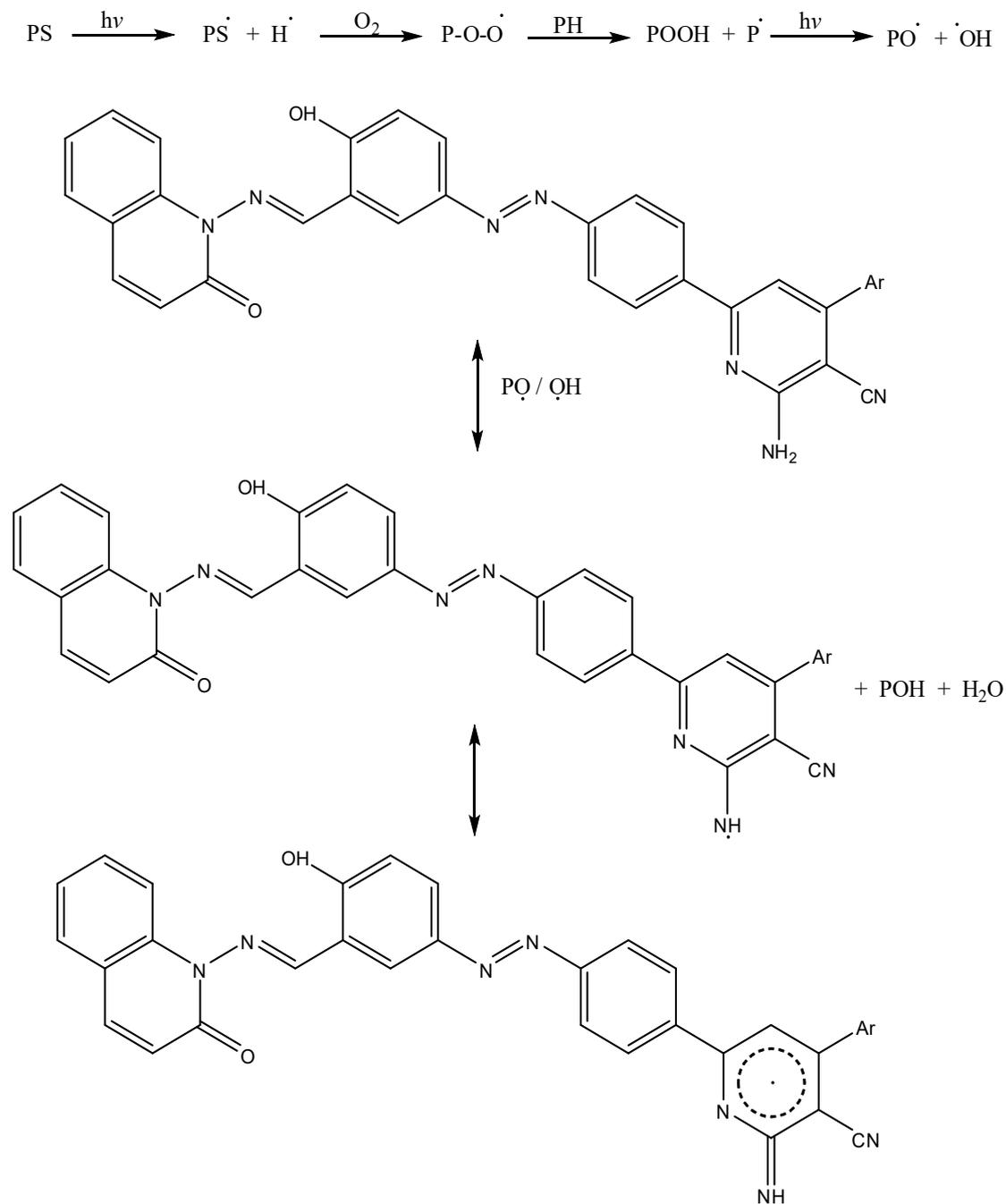


Figure 8 The suggested mechanism of photostabilization of PS by 2-amino pyridine derivatives a-e as radical scavenger.

Computational studies (DFT)

The theoretical results of the PS modification compounds showed that the total energy values of PS-D are higher energy content than the rest of the studied models showed that PS-D is more stable than other compounds depending on the following: Total energy. The values were as follows: -4412.94528 au for the

total energy. They can be arranged as follows: See **Table 1**. Depending on the different compensations for PS, we obtain 5 new compensations, see **Figure 9**.

PS-D > PS-A > PS-E > PS-B > PS-C

The negative sign in the HOMO energy indicates stability, that is, it is less effective, where values are shown (HOMO) PS-C is the least effective (stable) and PS-E is the most effective (unstable). It can be arranged as follows: See **Table 1**. It was necessary to know the electronic contributions of PS modification compounds for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), **Figures 10** and **11**.

PS-C > PS-A > PS-B > PS-D > PS-E

It also shows the values of (Gap energy), which is the energy of electronic excitation (the energy needed for excitation), as the more this increases Energy has increased stability PS-C is the most stable and PS-E is the least stable It can be arranged as follows: See **Table 1**.

PS-C > PS-A > PS-B > PS-D > PS-E

In the present study, all the quantum parameters were calculated for PS modification molecules. The quantitative values of the parameters are summarized in **Tables 1** and **2**. And the values of global softness (σ) with global hardness (η) in addition to the number fraction of electrons transferred (ΔN) for PS modification compounds are in agreement with experimental results. The resulting value of $\chi = 3.80732, 4.05204, 4.07477, 4.09136$ and 4.09136 as reported in **Tables 1** and **2**, shows the high number of electron transfer, which also confirms that PS modification compounds has the highest inhibition performance. The number of transferred electrons (ΔN) gives information about the number of electrons a molecule can transfer to the acceptor molecule.

The results of the (energy gap) values gave a range from 2.38453 eV for PS-C to 2.60277 eV. For PS-E, which proves that all PS modifications are conductive or semiconducting materials for electricity. The thermodynamic functions were calculated for the chemical design reactions, which are (reaction heat $\Delta_r H$, and entropy). Reactions for enthalpy of reaction, reaction entropy $\Delta_r S$, and compression-free energy $\Delta_r G$ (as in the general Eq. (9) According to the mathematical equations below: Using Eqs. (10) - (12), **Table 3** shows the following values.



$$\Delta_r H = \sum_{pro.} vH_m - \sum_{reac.} vH_m \quad (10)$$

$$\Delta_r S = \sum_{pro.} vS_m - \sum_{reac.} vS_m \quad (11)$$

$$\Delta_r G = \Delta_r H - T\Delta_r S \quad (12)$$

The values of $\Delta_r H$ were positive for all reactions, which indicates that they are endothermic reactions, while the values of $\Delta_r S$ were positive and the values of $\Delta_r G$ were negative, which was negative for all reactions, indicating that they are spontaneous. Hence the possibility of interaction occurring [17,18].

Table 1 Electronic energies and thermodynamic functions for all compounds using the DFT method.

Molecules	Enthalpy (H) (kcal mol ⁻¹)	Entropy (S) (cal mol ⁻¹ K ⁻¹)	Total energy (au)	E _{HOMO}	E _{LUMO}	Gap energy (E _{LUMO} - E _{HOMO})	Ionization potential (I)	Electron affinity (A)
Hydrogen molecule	7.847	31.132	-1.17548	-11.8086	+2.7235	14.5321	11.8086	2.7235
A	80.024	93.715	-956.45621	-6.49652	-2.42290	4.07362	6.49652	2.42290
B	91.803	87.180	-421.87464	-5.66160	+0.21660	5.8782	5.66160	0.21660
C	115.478	90.764	-366.12596	-4.90349	+0.41633	5.31982	4.90349	0.41633
D	61.233	78.776	-2803.17093	-6.68665	-0.36027	6.32638	6.68665	0.36027

Molecules	Enthalpy (H) (kcal mol ⁻¹)	Entropy (S) (cal mol ⁻¹ K ⁻¹)	Total energy (au)	E _{HOMO}	E _{LUMO}	Gap energy (E _{LUMO} - E _{HOMO})	Ionization potential (I)	Electron affinity (A)
E	61.229	76.230	-691.77457	-6.89319	-0.43021	6.46298	6.89319	0.43021
PS	277.540	202.236	-1610.96982	-5.58650	-2.55433	3.03217	5.58650	2.55433
PS-A	345.105	250.235	-2566.22306	-5.57344	-2.57610	2.99734	5.57344	2.57610
PS-B	357.049	244.190	-2031.65032	-5.57915	-2.52494	3.05421	5.57915	2.52494
PS-C	380.837	246.216	-1975.90435	-5.22921	-2.38453	2.84468	5.22921	2.38453
PS-D	326.411	232.897	-4412.94528	-5.59629	-2.58644	3.00985	5.59629	2.58644
PS-E	326.423	230.554	-2301.54868	-5.60201	-2.60277	2.99924	5.60201	2.60277

Table 2 Some physical values are calculated for all model (PS) modifications.

Subject	PS-A	PS-B	PS-C	PS-D	PS-E
Global hardness η	1.49867	1.5271	1.42234	1.50492	1.4996
Chemical softness σ	0.66725	0.6548	0.70307	0.66448	0.6668
Electronegativity χ	4.07477	4.05204	3.80732	4.09136	4.10239
Heat capacity (C _v) (Cal.mol ⁻¹ K ⁻¹)	151.790	147.544	149.214	137.881	137.700
Point group	C1	C1	C1	C1	C1
Dipole moment (Debye)	6.1806	8.8884	4.91625	8.27449	8.7339

Table 3 The values for (PS) modifications of the enthalpy of reaction (Δ_rH), the entropy of reaction (Δ_rS), and the Gibbs energy of reaction (Δ_rG) at room temperature.

Comp.	Δ_rH Kcal.mol ⁻¹	Δ_rS Cal. mol ⁻¹ .k ⁻¹	Δ_rG Kcal.mol ⁻¹
PS-A	3.238	16.548	-8.1574
PS-B	3.403	17.038	-8.4828
PS-C	3.516	15.48	-8.5958
PS-D	3.335	14.148	-7.5532
PS-E	3.351	14.466	-7.6640

Mulliken charges

The Mulliken charges have been impacted by the existence of the ring substituent, according to theoretical research for PS-C. See **Table 4** lists the computed Mulliken charges for PS-C. As can be seen, N (34) has the highest atomic charge, which is -0.76248, and N (64) has the lowest charge, which is -0.62781. These findings made it very evident that these 2 atoms are the most receptive to reactions and bonding [19]. More effective PS modification chemicals have been found to be able to share (give and receive) electrons with the metal, according to some recent studies.

Table 4 Mulliken charges for PS-C.

Atom	Charge								
1C	-0.17074	16N	-0.65415	31H	0.145701	46H	0.139903	61C	0.342444
2C	-0.08060	17O	-0.42931	32C	-0.09431	47H	0.131342	62N	-0.36909
3C	0.032401	18C	0.028813	33N	-0.24777	48N	-0.30669	63H	0.147187
4C	0.377443	19C	-0.13330	34N	-0.76248	49N	-0.29266	64N	-0.62781

Atom	Charge								
5C	0.537317	20H	0.130503	35H	0.333575	50C	-0.06744	65C	-0.23286
6H	0.141437	21C	-0.14114	36H	0.336861	51C	0.274624	66C	-0.23399
7H	0.163190	22C	-0.16464	37N	-0.48974	52C	-0.13287	67H	0.145633
8H	0.152481	23C	0.354932	38C	-0.15570	53C	-0.05382	68H	0.155109
9C	-0.17044	24C	-0.16383	39C	-0.07295	54C	0.144395	69H	0.155711
10C	-0.10050	25H	0.128783	40C	0.169503	55C	-0.10705	70H	0.155739
11C	-0.13528	26C	0.111644	41C	-0.11519	56H	0.153662	71H	0.144916
12C	-0.11716	27C	0.432775	42C	-0.15166	57H	0.166801	72H	0.159685
13H	0.164804	28C	0.154706	43C	0.071366	58H	0.172727	73H	0.124529
14H	0.142033	29C	-0.17271	44H	0.160320	59O	-0.62198		
15H	0.137123	30C	0.070246	45H	0.159198	60H	0.418410		

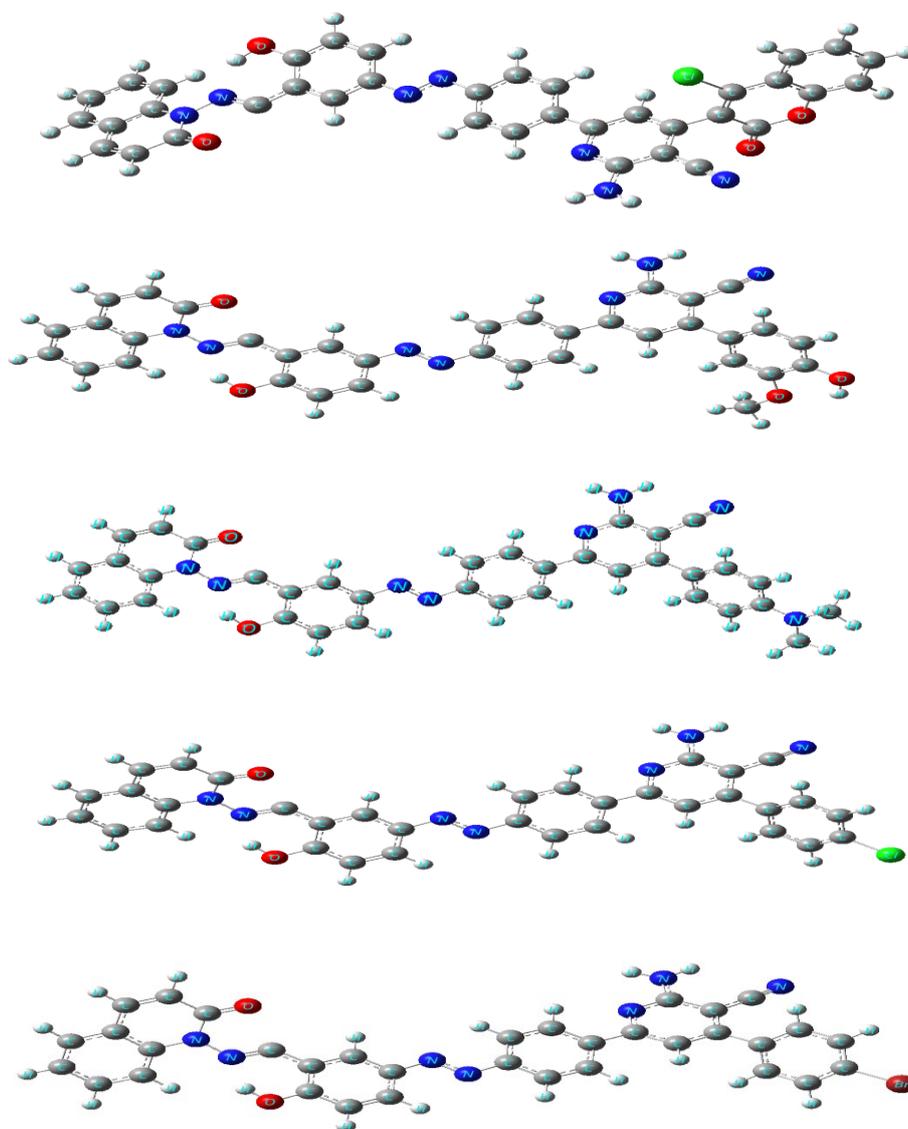


Figure 9 The geometric molecular structure for models (PS) modifications.

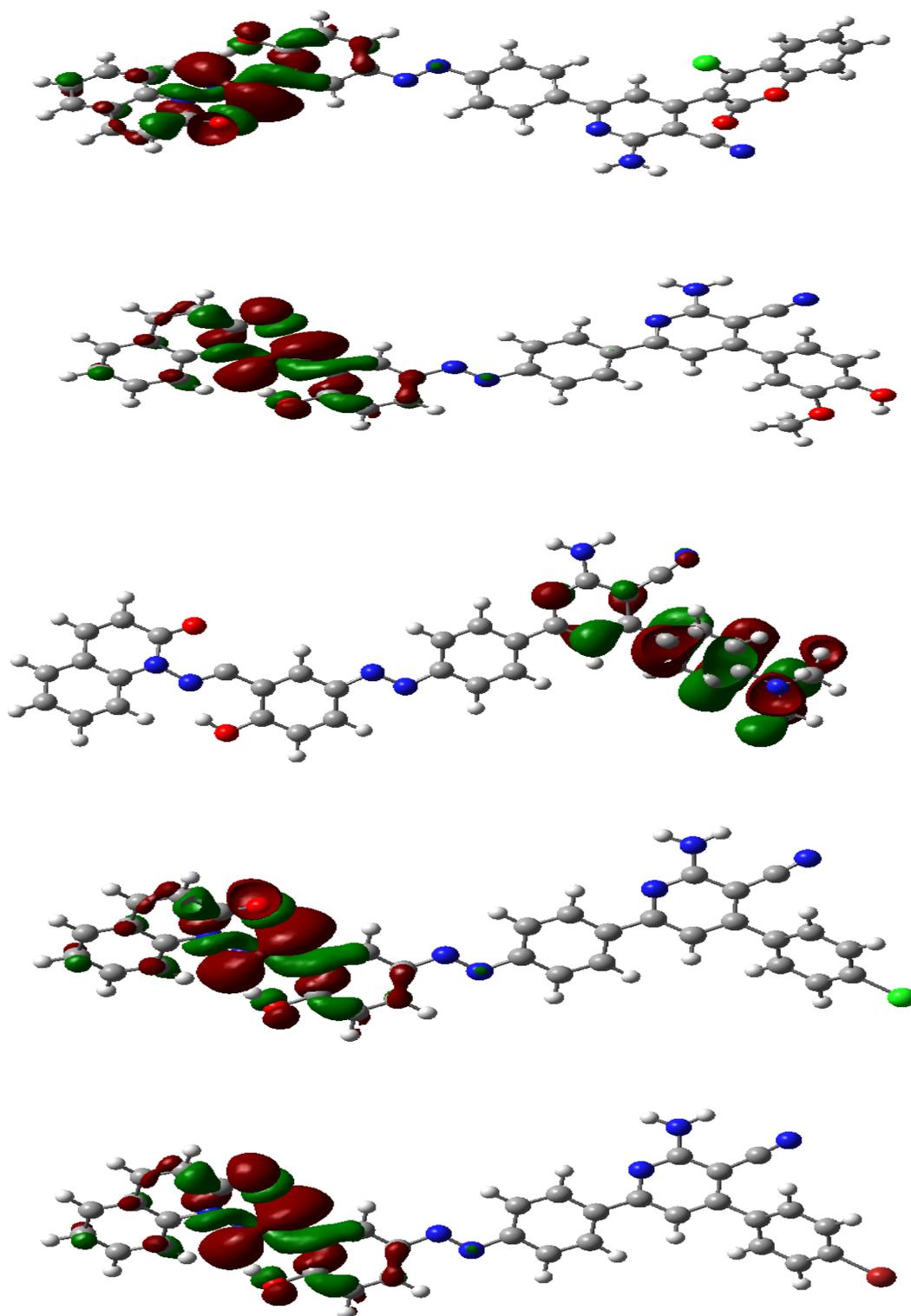


Figure 10 Atomic contributions in the highest occupied molecular orbital (HOMO) for models (PS) modifications.

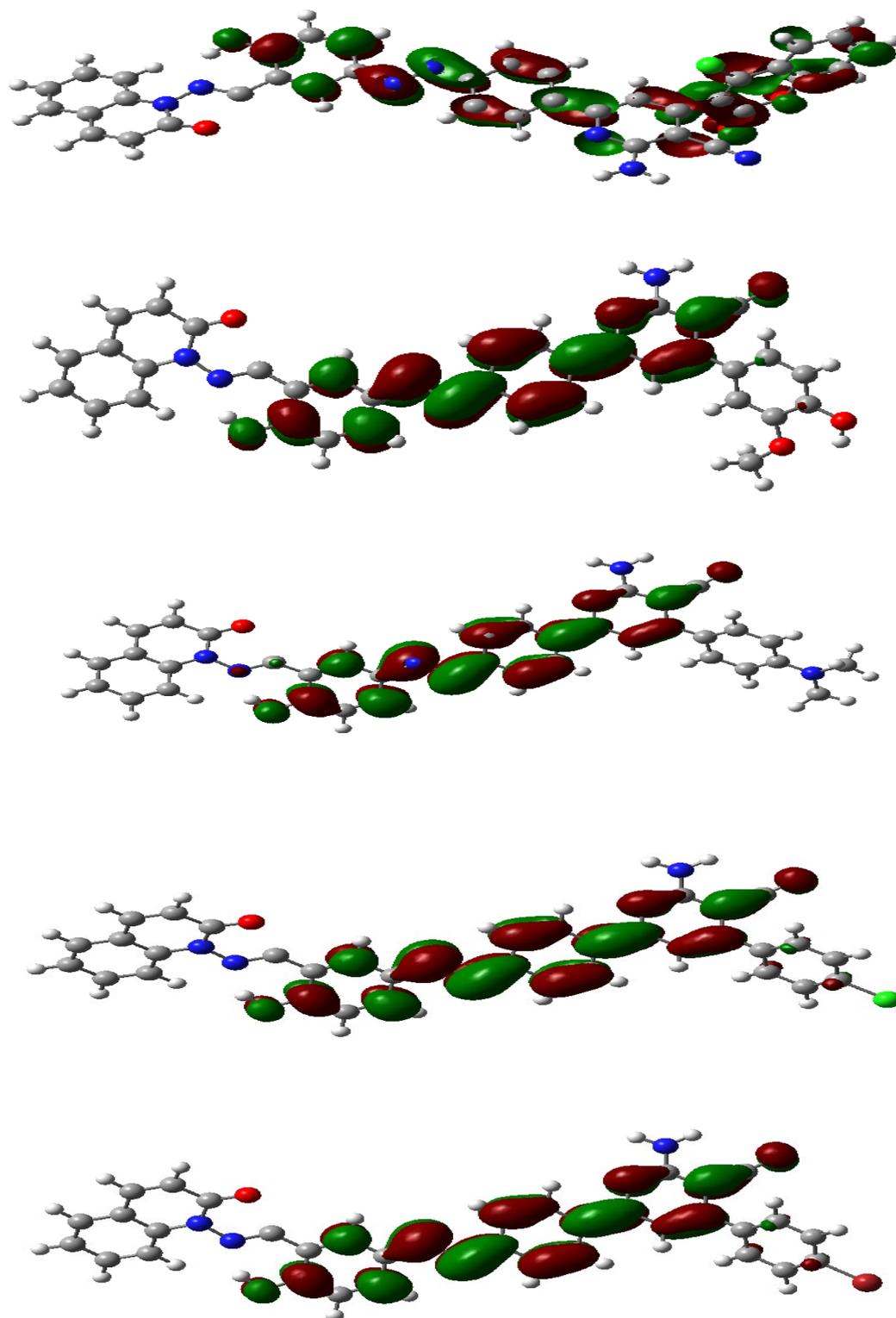


Figure 11 Atomic contributions in the lowest unoccupied molecular orbital (LUMO) for models (PS) modifications.

Conclusions

In the research presented in this publication, chemicals with 2-amino pyridine derivatives were used to study the photostabilization of PS films. For PS films, these chemicals function effectively as photostabilizers. These supplements Through UV absorption or screening, FTIR spectra, weight loss, and optical microscopy, the PS films are stabilized. According to the aforementioned processes and photostability, compound (a) was found to be the most effective in the photostabilization process. The use of molecules (a-e) that are 2-amino pyridine derivatives is encouraged by these mechanisms.

Acknowledgments

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