

Photostabilization of PVC films by using some novel tetra Schiff's  
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## Photo stabilization of PVC films by using some novel tetra Schiff's bases derived from 1,2,4,5-tetra-[5-amino-1,3,4-thiadiazole-2-yl]-benzene

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### Abstract

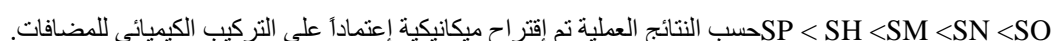
A five new Schiff's bases namely 1,2,4,5-tetra[5-arylidene-1,3,4-thiadiazole-2-yl]-benzene are synthesized by condensation of 1,2,4,5-tetra-[5-amino-1,3,4-thiadiazole-2-yl]-benzene with four equivalent of appropriate aromatic aldehyde in ethanol. The compounds are characterized by analytical and spectral means. The activity of these compounds in photostabilization of PVC is investigated using FTIR and UV-VIS Spectrophotometric techniques. All these additives were act as stabilizer in PVC film. The following trend is obtained for the photostabilization effect of PVC films in the presence of these additives.



According to the experimental results obtained, a propose mechanism was suggested depending on the structure of the additive.

### الخلاصة

تم في هذا البحث تحضير خمساً من قواعد شف الجديدة المسماة (-1,3,4-thiadiazole-2-yl]-5-arylidene-1,2,4,5-tetra- (benzene) - (1,2,4,5-tetra-[5-amino-1,3,4-thiadiazole-2-yl]-benzene) مع أربع كميات مكافئة من الديهايدات أروماتية. تم تشخيص المركبات المحضرة باستخدام الوسائل التحليلية والطيفية. وتم قياس فعاليتها كمثبتات ضوئية لمادة (PVC) تقنيات الأشعة تحت الحمراء وفوق البنفسجية. جميع هذه المضافات عملت كمواد مثبتة للـ (PVC). فعالية هذه المواد كمثبتات كانت كما يلي



## Introduction

Synthetic polymers such as plastics are extensively used in building construction and other outdoor applications where they are routinely exposed to sunlight. There is a great interest at present in the photo-oxidative degradation of polymeric materials because macromolecules have increasingly widespread commercial applications. Polymeric materials, synthetic, semisynthetic and natural are photodegradable when exposed to the environment(1-3).

The photostabilizing effect of mono Schiff base in films of PVC had been studied(4-6). To our knowledge there is no attempt to investigate the photostabilization of PVC films by tetra Schiff bases compounds containing four 1,3,4-thiadiazole rings, therefore, in this work we report the designing of some new Schiff bases (Scheme 1) and studying their use as photostabilizing reagent with the hope that the incorporation of four 1,3,4-thiadiazoles ring and four azomethine groups may act as an excellent UV absorber.

## Experimental

### Materials

#### 1. Synthesis of 1,2,4,5-tetra [-5-amino-1,3,4-thiadiazole-2-yl-] benzene[1]:

A mixture of pyromelitic acid (0.01mol) and (0.04mol, 3.64 g) of thiosemicarbazide with (15 mL) of phosphorusoxy chloride was refluxed gently for (5hrs.). After cooling, (125 mL) of water was added, the mixture was then refluxed for (10 hrs.), filtrated, and neutralized with potassium hydroxide. The precipitate was washed with water and recrystallized from (ethanol-water) to give the desired product yielding (64- 65%).

#### 2. Synthesis of 1,2,4,5-tetra-[-5-arylidene-1,3,4-thiadiazole-2-yl]-benzene:

A mixture of 1,2,4,5-tetra-[5-amino-1,3,4-thiadiazole-2-yl]-benzene (0.01 mol) and appropriate aromatic aldehyde(0.04 mol) was dissolved in (35 mL) of absolute ethanol. The mixture was then refluxed for (7 hrs.) with stirring. After cooling to room temperature the precipitate was filtered, dried, and recrystallized from ethanol yielding (75%).

## Experimental Techniques

### Films Preparation

A Poly(vinyl chloride) solution (5 g/100 ml) in tetrahydrofuran (THF) was used to prepare different thickness of polymer films, (measured by a micrometer type 2610 A, Germany) with 0.5% of the compounds prepared. The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stand specially used for irradiation which is aluminum plate (0.6 mm) in thickness supplied from (Q-panel) company.

### Irradiation experiment

#### Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Philips, Germany), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and another one behind. Each side contains lamps type (Fluorescent Ultraviolet Lights) 40 watt each. The lamps are of the type (UV-B 313) giving spectrum range between (290-360 nm) with the maximum wavelength being at (313 nm).

The polymer film samples vertically fixed and parallel to the lamps to be sure that UV incident radiation is vertically incident on the samples, the irradiation samples are changed places from time to time to be sure that the intensity of light incident on all sample is equal.

### III. Measuring the photodegradation rate of polymer films using infrared spectrophotometry

The photodegradation of polymer film samples were followed by mentoring of FTIR spectra in the range (4000-400)  $\text{cm}^{-1}$  the spectra were recorded using FTIR 8300 Shimadzu Spectrophotometer .

The position of carbonyl absorption is specified at 1722  $\text{cm}^{-1}$ , and polyene group at (1602  $\text{cm}^{-1}$ ) (7).

The photodegradation during different irradiation times were followed by observing changes in carbonyl and polyene peaks. Then carbonyl (Ico) and polyene (Ipo) indices were

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calculated by comparison of the FTIR absorption peaks at 1722 cm<sup>-1</sup> and 1602 cm<sup>-1</sup> with reference peak at 1328 cm<sup>-1</sup>, respectively. This method is called band index method(7) which includes:

$$I_s = \frac{A_s}{A_r} \dots\dots\dots(1)$$

A<sub>s</sub> = Absorbance of peak under study.

A<sub>r</sub> = Absorbance of reference peak.

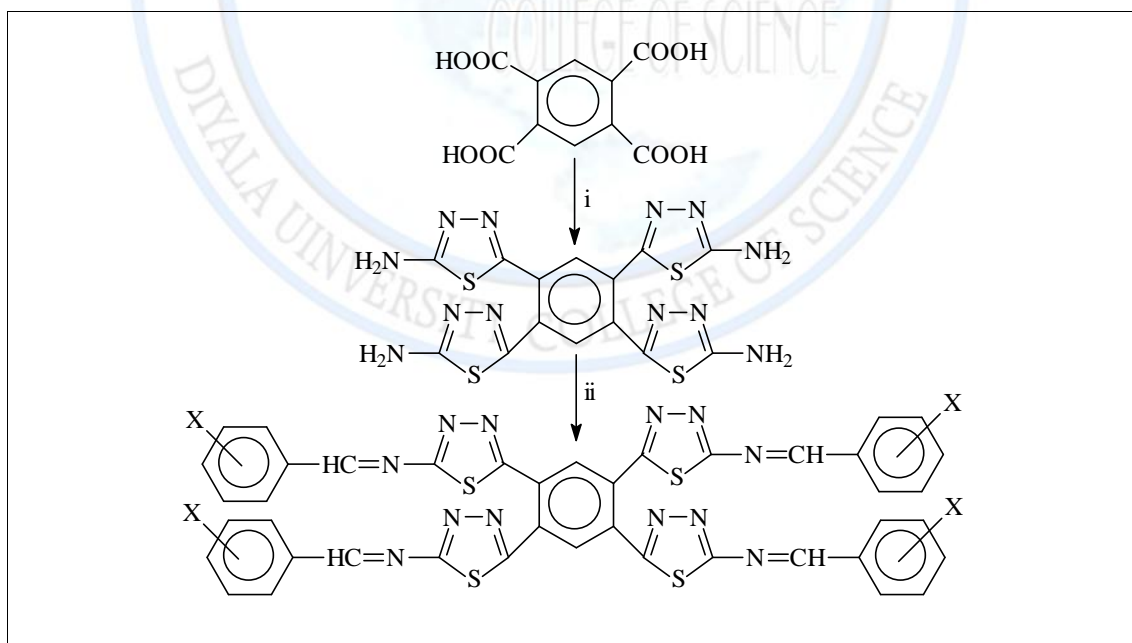
I<sub>s</sub> = Index of the group under study.

Actual absorbance, the difference between the absorbance of base line and top peak (A Top Peak – A Base Line), is calculated using the Base Line method(8. (

## Results and Discussion

### Stepwise synthesis of materials

The synthesis of the target 1,2,4,5-tetra[5-arylidene-1,3,4-thiadiazole-2-yl]- benzene are shown in the sequences of reactions depicted in Scheme (1).



**Scheme (1): Reagent and conditions: (i) thiosemicarbazide, POCl<sub>3</sub>, reflux (5hours); (ii) appropriate aromatic aldehyde, absolute ethanol, reflux (24hours).**

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The synthesis of 1,2,4,5-tetra-[5-amino-1,3,4-thiadiazole-2-yl]-benzene was achieved by the reaction of pyromelic acid with four equivalents of thiosemicarbazide in the presence of phosphorus oxychloride. The authenticity of the product was confirmed by spectral (UV-VIS and FTIR) data. The FTIR spectrum of this compound show two strong broad bands at (3267 and 3099 $\text{cm}^{-1}$ ) attributable refer to stretching frequency for of (-NH<sub>2</sub>) vibration. The broadening may be attributed to intermolecular hydrogen bonding. Moreover, the spectrum showed the following characteristic bands at (1610 $\text{cm}^{-1}$ ) cyclic system(C=N) for 1,3,4-thiadiazole ring, (1515 and 1463  $\text{cm}^{-1}$ ) for (C=C) for the aromatic ring, (1031 $\text{cm}^{-1}$ ) for (N-N) vibration, and (829  $\text{cm}^{-1}$ ) tetra substituted benzene, these data supported the validity of this compound.

The additives 1,2,4,5-tetra-[5-arylidene-1,3,4-thiadiazole-2-yl]-benzene were prepared by refluxing the compound with four equivalent Quantities of appropriate aromatic aldehyde in absolute alcohol for overnight. The constitution of additive compounds was supported by their spectral data.

The IR spectra shows an absorption bands at (1600 – 1650  $\text{cm}^{-1}$ ) which were assigned to (C=N) stretching frequency of the Schiff base additive formed as well the other informative bands are listed in Table(1.)

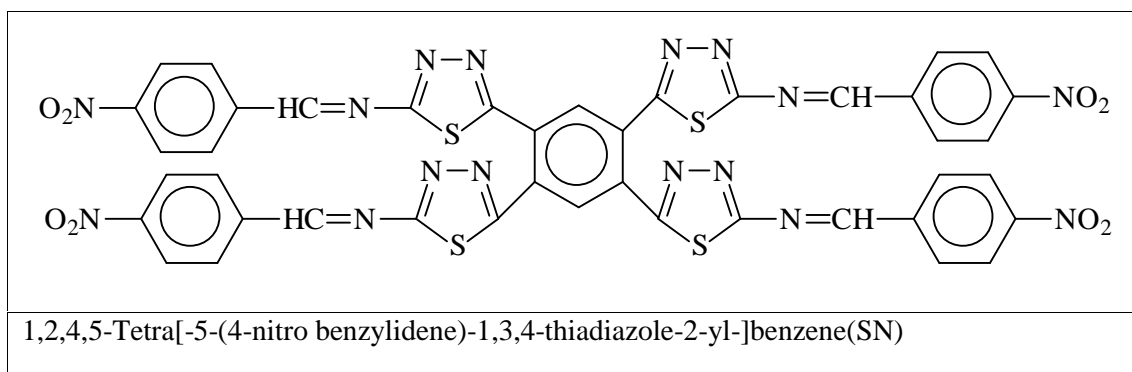
**Table (1): Characterization of the synthesized compounds**

Compound	Formula	M.Wt gm/mole	% Yield	M.P. C°	Wave number $\text{cm}^{-1}$	
					C=N	C-H <sub>aromatic</sub>
1	C <sub>14</sub> H <sub>10</sub> N <sub>12</sub> S <sub>4</sub>	474.57	60	>360	1610	3100
SN	C <sub>42</sub> H <sub>22</sub> N <sub>16</sub> O <sub>8</sub> S <sub>4</sub>	1006.99	62	220	1615	3090
SP	C <sub>42</sub> H <sub>26</sub> N <sub>12</sub> S <sub>4</sub>	827	65	200	1608	3095
SH	C <sub>42</sub> H <sub>26</sub> N <sub>12</sub> O <sub>4</sub> S <sub>4</sub>	891	60	>360	1620	3000
SO	C <sub>42</sub> H <sub>26</sub> N <sub>12</sub> O <sub>4</sub> S <sub>4</sub>	891	65	>360	1610	3010
SM	C <sub>46</sub> H <sub>34</sub> N <sub>12</sub> S <sub>4</sub>	883.11	70	235	1612	3110

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1,2,4,5-Tetra[5-benzylidene-1,3,4-thiadiazole-2-yl]benzene(SP)
1,2,4,5-Tetra[5-(4-methyl benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SM)
1,2,4,5-Tetra[5-(4-hydroxy benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SH)
1,2,4,5-Tetra[5-(2-hydroxy benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SO)

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**Fig (1): The chemical structure of the prepared compounds.**

The following Compounds, 1,2,4,5-Tetra[5-benzylidene-1,3,4-thiadiazole-2-yl]benzene(SP), 1,2,4,5-Tetra[5-(4-methyl benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SM), 1,2,4,5-Tetra[5-(4-hydroxy benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SH), 1,2,4,5-Tetra[5-(2-hydroxy benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SO) and 1,2,4,5-Tetra[5-(4-nitro benzylidene)-1,3,4-thiadiazole-2-yl]benzene(SN) can be used as photostabilizer. In order to study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PVC and with additive films with light of wavelength,  $\lambda = 313 \text{ nm}$  led to a new change in their FTIR spectrum, the appearance of bands in  $1772 \text{ cm}^{-1}$  and  $1724 \text{ cm}^{-1}$  respectively, are attributed to the formation of carbonyl groups related to chloroketone and the second one is due to aliphatic ketone respectively, together with formation of a band at  $1604 \text{ cm}^{-1}$  attributed to polyene group(9).

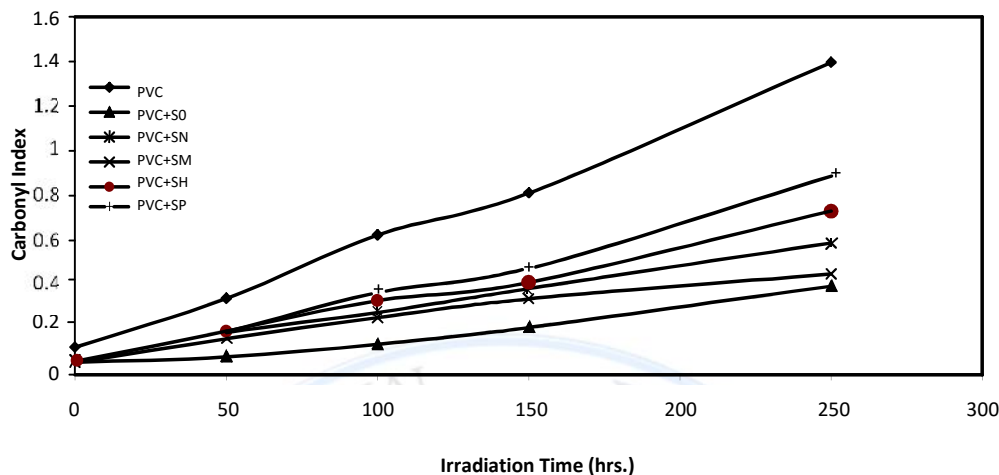
The absorption of the polyene and carbonyl groups are used to follow the extend of polymer degradation during irradiation. This absorption was calculated as carbonyl index (Ico) and polyene index (IPO). Therefore, one should expect that the growth of carbonyl index is a measure to the extent of degradation. As seen from Figure (1) that the presence of SP, SH, SM, SN and SO show lower growth rate of carbonyl index with irradiation time with respect to PVC film without additives (control).

As shown in Figure (2), the growth of carbonyl index with irradiation time is lower than PVC control. So, these additives might be considered as photostabilizers of PVC polymer.

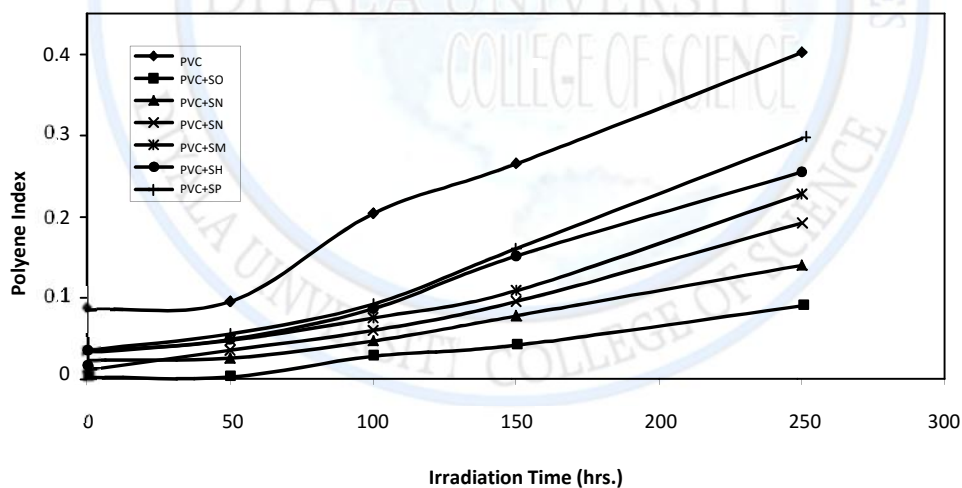
The efficient photostabilizer show a longer induction period. Therefore, from Figure (2), the SO is the most active photostabilizer, followed by SN, SM. SH and SP which is less active. As it was mentioned before polyene compounds are produced during photodegradation of

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PVC. Therefore, polyene index (IPO) was monitored with irradiation time and the presence and absence of these additives. Results are shown in Figure (3).



**Fig (3): The relationship between the carbonyl index and irradiation time for PVC films (30  $\mu\text{m}$ ) thickness containing different additives, concentration of additives are fixed at 0.5% by weight.**



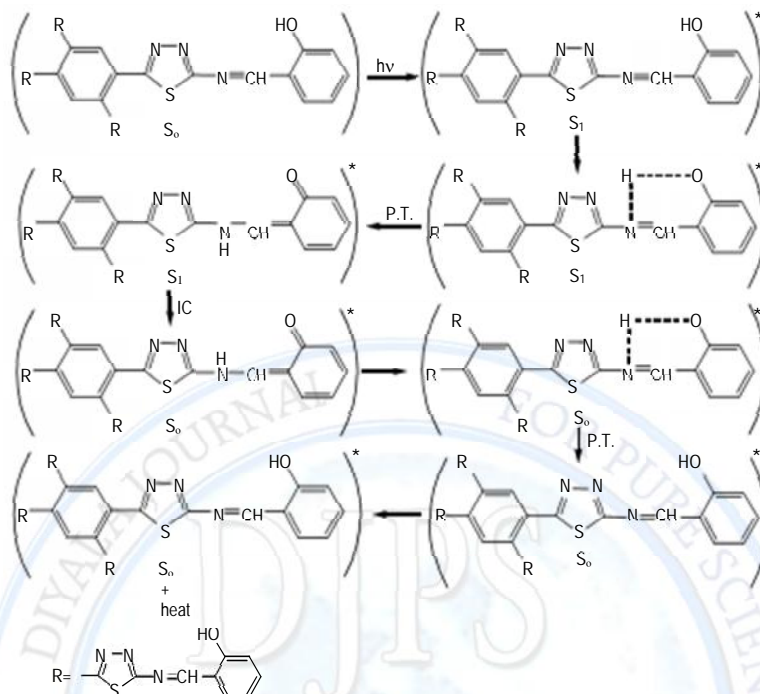
**Fig (3) The relationship between the polyene index and irradiation time for PVC films (30  $\mu\text{m}$ ) thickness containing different additives, concentration of additives are fixed at 0.5% by weight.**

The most probable mechanism involved in a photostabilization is the change energy of absorbed photon to the intramolecular proton transfer. This reaction may occur by two proposed cycles Scheme (2) and (3), the first shows the intersystem crossing (ICS) process to

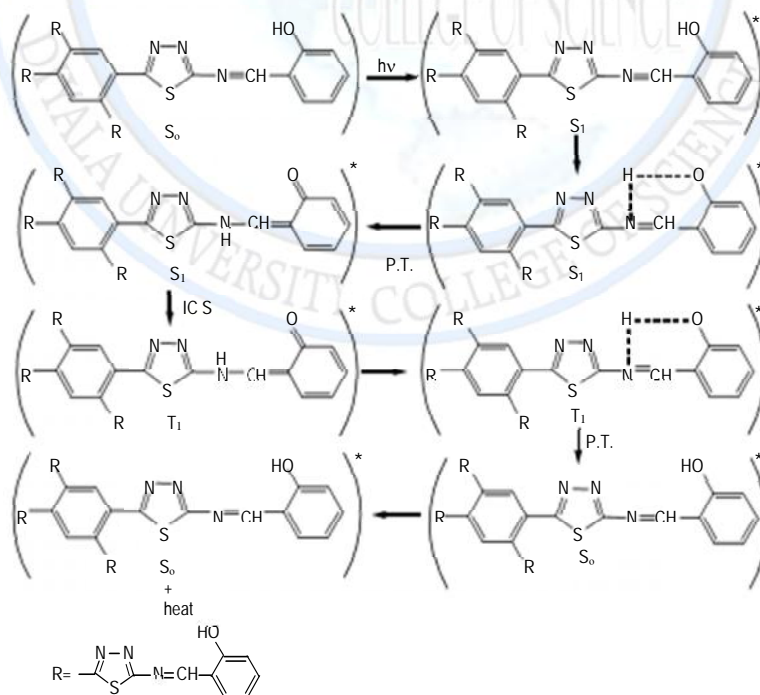


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the excited triplet state, while the second is referred to of internal conversion (IC) process to the ground state.



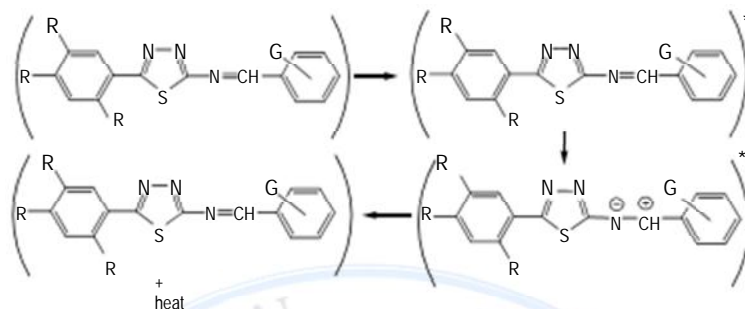
**Scheme (2): Suggested mechanism of photostabilization of 2,5-di(arylhydrazones)-1,3,4-thiadiazole compounds through absorption of UV light and dissipation light energy as heat.**



**Scheme (3): Suggested mechanism of photostabilization of PVC 2,5-di(arylhydrazones)-1,3,4-thiadiazole compounds through absorption of UV light and dissipation light energy as heat.**

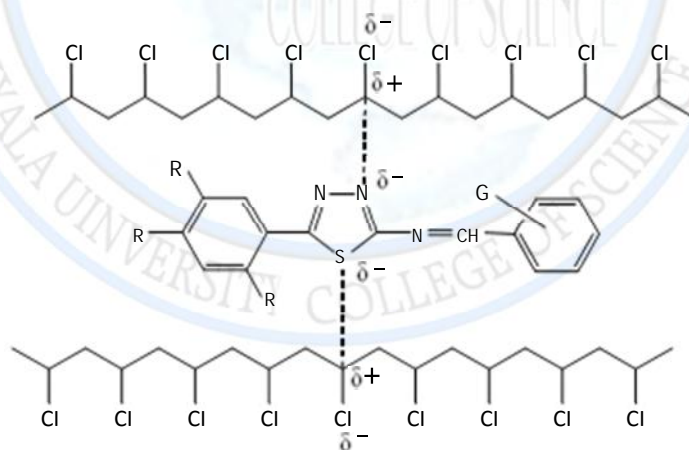
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Other mechanism(9) explains the use of these compounds as photostabilizer by charge separated species which could be in form the excited state such a structure would allow dissipation of energy through rotation on increased vibration about the central bond.



**Scheme (4): Suggested mechanism of photostabilization of 2,5-di(arylhydrazones)-1,3,4-thiadiazole compounds through absorption of UV light and dissipation light energy as heat.**

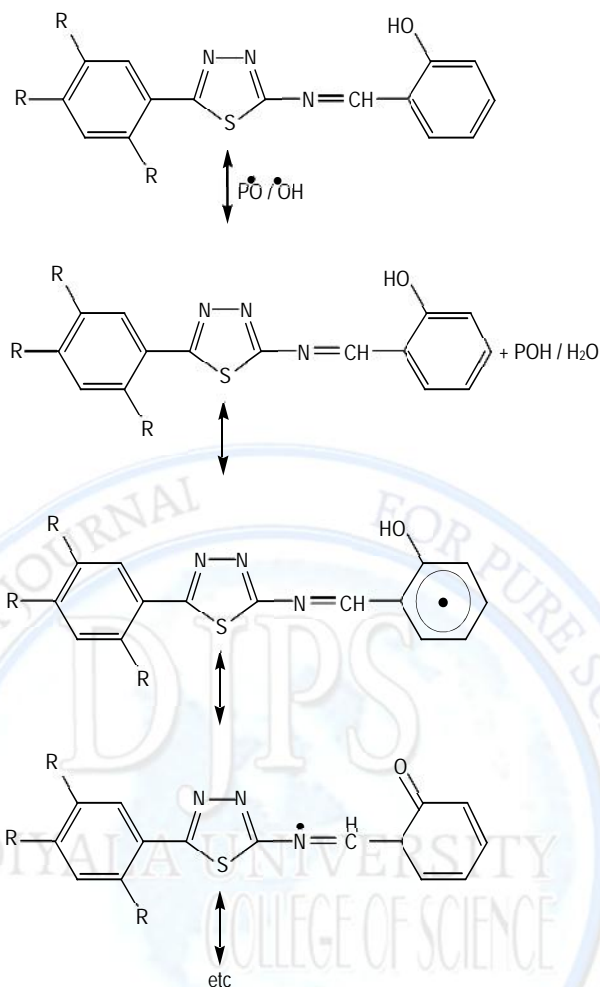
1,3,4-Thiadiazole ring has two different atoms of different electronegativity such as nitrogen and sulfur. The polarity of this ring explains the attraction between the stabilizer and PVC Scheme (5). This mechanism can lead to the conclusion that crosslinking could be takes place upon UV irradiation, which may be correct for all compounds.



**Scheme (5): Suggested mechanism of photostabilization of 2,5-di(arylhydrazones)-1,3,4-thiadiazole compounds through the interaction between PVC and Schiff base compounds.**

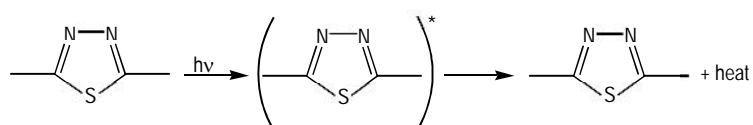
The hydroxyl group of the additive might acts as radical scavenger for photostabilization process. Therefore this Schiff bases, besides acting as UV absorber they may also act as radical scavenger additives. Scheme (6).

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**Scheme (6): Suggested mechanism of photostabilization of PVC 2,5-di(2-hydroxyphenyl)hydrozn)-1,3,4-thiazole compounds as radical scavenger .**

The rings of 1,3,4thiadiazole play a role in the mechanism of the stabilizer process by acting as UV absorber. The UV light absorption by these additives containing 1,3,4 thiadiazole dissipates the UV energy to harmless heat energy Scheme (7) Furthermore, this ring plays a role in resonating structures conjugation of radical in peroxide decomposer Scheme (7), which supprt it function as a photostabilizer and this mechanism was in agreement with that obtained by Emad et al.(10)



**Scheme (7): Suggested mechanism of photostabilization of 1,3,4-thiadiazole as UV absorber.**

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