The use of new pyridine derivatives as effective photostabilizers for poly (vinyl chloride)

Sarah Abdulhamza Hameed, Hiba H. Ibraheem and Emad Yousif

1Chemistry Division, Department of Applied Science, University of Technology/Baghdad, Iraq
2Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq
*Corresponding Author :dr.hiba1982@gmail.com

Abstract: This work included synthesis of several new pyridine derivatives by cyclization of compound (3) with appropriate aromatic aldehydes (4-Chloro-3-formylcoumarin, 4-bromobenzaldehyde, 4-chlorobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-N,N-dimethylaminobenzaldehyde) in presence of malononitrile and ammonium acetate to obtain pyridine derivatives (5a-e). The new synthesized compounds have been characterized using Melting point, TLC, FT-IR spectroscopy and 1H-NMR. Five new pyridine derivatives have used like inhibitors until Poly(vinyl chloride) (PVC) photodegradation. The pyridine derivatives have added into PVC onto a concentration from 0.5% through weight. The PVC thinlayers (40µm thickness) have irradiated onto room temperature through ultraviolet (UV) light into up into 300 h. The changes within PVC thinlayers after irradiation have monitored through Fourier transform infrared spectroscopy, weight lack, while atomic strength microscopy. These alterations have quite remarkable within the empty PVC thinlayers liken into the ones gained when Active substances have utilized. The pyridine derivatives have prevent the PVC photodegradation during immediate absorption from UV light, interfere through PVC chains, while touching like radical tie up while proton transfer action into stabilize the polymeric compounds.

Keywords: Poly(vinyl chloride), 2H-chromen-2-one, pyridine.

1. Introduction

Pyridine is one of the heterogeneous organic compounds of chemical formula C₅H₅N. In many aspects it can be relative to well established while very fundamental aromatic molecule, benzene, with one C-H group exchange by a nitrogen atom. Pyridines like benzene contain a conjugated system of six π-electrons., that are delocalized over the heterocyclic ring. The molecule is planar in nature and follows Huckel criteria for aromaticity [1]. Pyridine is liquid in nature, colourless. The boiling point of pyridine is 115.2 °C and its freezing point is −41.6°C. Its density, 0.9819 g/cm³, is close to that of water, and its refractive index is 1.5093 at a wave length of 589 nm and a temperature of 20°C [2]. Pyridine is a weakly basic heteroaromatic compound. Pyridine can be mixed with almost all organic compounds, as well as mixed with water [3]. Pyridine derivatives have been reported for variety of biological activities and number of the compounds are in clinical uses. Pyridine has conjugated system π-electrons exactly as benzene has, that are delocalized over the heterocyclic ring [4].

PVC is used in many industries, either rigid or flexible, white or black, and a wide range of colors between them. It provides many necessary products and is considered a durable and long-lasting building material. [5] . PVC was accidentally synthesized in 1872 as a white solid in a bottle of vinyl chloride, which left its exposition by German chemist Eugen Baumann [6]. Polyvinyl chloride is considered one of the most produced and consumed polymers in the world and it has many applications. However, exposure of polyvinyl chloride to sunlight for a long time or high temperature leads to photo degradation [7]. Heat,
mechanical energy, radiation, and ozone are among the main factors causing degradation leading to various kinds like thermal, thermo oxidative, photo degradation, chemical, biological, hydrolytic while degradation by irradiation. In a depolymerization reaction, a reversal of polymerization occurs which includes initiation at chain ends, propagation, Termination [8]. Mineral soaps and organic tin compounds are highly effective polymeric additives for thermal stabilization, some of which are considered toxic and cause environmental problems, some of which leave toxic residues during the decomposition process and in recent times organic stabilizers are used [9].

This investigation demonstrated synthesis from new five pyridine derivatives compounds derived for Quinolone with fully characterization, while aiming into be efficacious stabilizers versus the photodegradation from PVC paradigms. Reaction sequences of the synthesized compounds are appeared within figure (1).
Figure 1. Reaction sequences of the synthesized compounds.
Figure 2. Structure of compounds (5a-e).
2. Experimental

2.1 Synthesis of 1-aminoquinolin-2(1H)-one (1)

A mixture of 2H-chromen-2-one (0.02 mole) within ethanol (25 ml), hydrazine hydrate (80%) (1 g, 0.02 mole) is added drop wise for stirring [10]. The mixture was refluxed for 24 hrs. After cooling the solid formed, is filtered off, while recrystallized from ethanol:water (1:1) to give of compound (1), white outcome, yield 88%, M.P (136-138°C).

2.2 Synthesis of Azo Derivative (2)

Ethyl 4- aminobenzoate or 4-amino acetophenone (0.01 mole) was added to the concentrated hydrochloric acid (4.5 ml) and a mixture from water (4 ml). The product mixture was stirred into (10 min), cooling the solution to (0-5) 0°C. Added dropwise water (2.5 ml) to a sol of solution of sodium nitrite (0.69 g, 0.01 moles) with stir for ten min, added dropwise. The product sol of diazonium salt to a mix from salicylaldehyde (1.22 g, 0.01 moles) within ethanol and 10% NaOH (ten ml.) in (0-5)0°C in pH=5.5 while disappearing from reactants was figured as stated by to TLC technique. Later the adding was finished, the mixture was stirred until further 20 min. After that it was left until (1 hr). The rigid created was filtrated off while dry while recrystallizing of ethanol to get the compound (2), orange outcome, yield 84%, M.P (104-106°C) [11].

3.3 Synthesis of Schiff base compound (3)

A mixture of (0.01 mole) of compound (1) in (10 ml) of absolute ethanol, and compound (2) (0.01 mole) was refluxed for 12 hours within the presence from (3-4) drops of glacial acetic acid. The reaction was monitored through TLC (hexane: ethylacetate, 7:3, Rf = 0.61). After cooling the outcome, a solid formed, was filtered, dried while purified through recrystallized from ethanol [12], dark orange precipitate, yield 54%, M.P (218-220°C).

2.4 Synthesis of 4-Chloro-3-formylcoumarin (4)

A mixture of 4-hydroxycoumarin (1.4 gm, 0.007 mole) in dry DMF (40 ml) was added dropwise to POCl₃ (3.7 ml, 0.01 mole) in dry DMF (8 ml, 0.1 mole) at room temperature. The reaction mixture was then stirred for 1 hr. at room temperature and heated at reflux temperature for 2 hrs. at 60 °C., the progress of the reaction was monitored by TLC (hexane:Ethyl acetate, 7:3, Rf = 0.77). After the reaction is completed, the mixture was poured onto crushed ice (100 gm.) under vigorous stirring. The formed precipitate is filtered off to give compound (4) [13] and recrystallized from ethanol:water 1:1. Yellow consequence, yield 74%, M.P (122-124°C).

2.5 Synthesis of Compounds (5a-e)

A solution from compound (3) (0.002 mole) within ethanol (15 ml.) with appropriate aromatic aldehydes (4- Chloro-3-formylcoumarin (4), 4-bromobenzaldehyde, 4-chlorobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-N,N-dimethylaminobenzaldehyde ) (0.002 mole), malononitrile (0.002 mole) and ammonium acetate (1.2 g, 0.016 mole) have been putted [14]. The reaction medley has refluxed until 12 hrs while the demise from reactants has figured approving into TLC technique. The solid formed was filtered off then rinsed with water, dehydrated while recrystallized from ethanol into get outcome compounds (5a-e).

2.5.1 Synthesis of 2-amino-4-(4-chloro-2-oxo-2H-chromen-3-yl)-6-(4-((E)-(4-hydroxy-3-((E)-(2-oxoquinolin-1(2H)-ylimino)methyl)phenyl)diazenyl)phenyl) nicotinonitrile (5a)

Melting point: 258-260 °C, brown precipitate, Yields: 70%. TLC (hexane:Ethyl acetate, 7:3, Rf = 0.6).
2.5.2 Synthesis of 2-amino-4-(4-bromophenyl)-6-(4-((E)-(4-hydroxy-3-((E)-(2-oxoquinolin-1(2H)-ylimino)methyl)phenyl)diazenyl)phenyl)nicotinonitrile (5b)

Melting point: 316-318 °C, orange precipitate, Yields: 65%. TLC (hexane:Ethyl acetate, 7:3, Rf = 0.7).

2.5.3 Synthesis of 2-amino-4-(4-chlorophenyl)-6-(4-((E)-(4-hydroxy-3-((E)-(2-oxoquinolin-1(2H)-ylimino)methyl)phenyl)diazenyl)phenyl)nicotinonitrile (5c)

Melting point: 322-324 °C, dark brown precipitate, Yields: 60%. TLC (hexane:Ethyl acetate, 7:3, Rf = 0.68).

2.5.4 Synthesis of 2-amino-4-(4-(dimethylamino)phenyl)-6-(4-((E)-(4-hydroxy-3-((E)-(2-oxoquinolin-1(2H)-ylimino)methyl)phenyl)diazenyl)phenyl)nicotinonitrile (5e)

Melting point: 288-290 °C, orange precipitate, Yields: 78%. TLC (hexane:Ethyl acetate, 7:3, Rf = 0.8).

2.6 Films Preparation

The preferable solvent until PVC is tetrahydrofuran. Fixed concentration from PVC solutions (5%) within THF was used into prepare polymer films for 40 micro meter thickness through evaporation technique onto room temperature until 24 hrs. The prepared organic compounds (0.5% concentration through weight ) were putted into the thinlayers starting onto zero concentration (empty). It was necessary into control the hygrometry while the rate from evaporation from solvent during casting into maintain good optical quality and very limited turbidity. After completing dissolution, the resulting solution was spread within glass frame while left overnight. This frame was made through glue the laboratory glass slide within a piece from regular glass, into obtain tiny sinks, their volume is (4 ml) [15]

2.7 Accelerated Testing Technique

A UV Light (λ max = 313 nm with light density = 6.2 × 10⁻⁹ ein⁻³.dm⁻¹.s⁻¹ nm) has utilized into stimulate the PVC thin layers utilizing a quickened weatherometer QUV fitter (Philips, Saarbrücken, Germany) at 24 degrees Celsius. The PVC film was alternated every now and then into ensure during whole aspects.

2.8 Photodegradation Rate (kd) of PVC

2.8.1 FTIR spectroscopy method

Photodegradation from PVC thin layers were tracked through FTIR 4200 JASCO spectrophotometer (4000-400) cm⁻¹. Ultraviolet radiation from polymeric additives was working into alterations during those chemical, mechanistic while physical particulars [16]. Photo-oxidation from PVC commands into the forming from carbonyl, combined double bonds, while hydroxyl totals[17]. Thus, the alterations during IR assimilation bands until carbonyl (1722 cm⁻¹ ), polyene (1602 cm⁻¹ ) while hydroxyl (3500 cm⁻¹ ) totals have tracked while resembled into a base peak (1328 cm⁻¹ ). The indicators until carbonyl (I C=O ), polyene (I C=C ) while hydroxyl (I OH ) assorptions have elaborated utilizing band index method Equation (1). The elaborate assortion index (I s) has vassal within jointly the absorbance from peak under study (A s ) while that until the indication peak (A r ) [18].
\[ I_s = \frac{A_s}{A_r} \quad (1) \]

### 2.8.2 Through Weight Loss

The weight damage proportion for PVC specimens within irradiation practicability have studied utilizing for the weight from PVC specimen prior (W1) while next radiation (W2) utilizing Equation (2).

\[ \text{Weight loss\%} = \left(\frac{W1 - W2}{W1}\right) \times 100 \quad (2) \]

### 3. Results and Discussion

A number of ketone derivative are well known for their useful as starting material for synthesizing of another compounds, so for this purpose some ketone derivative (3) which was prepared by condensation reaction between 1-aminoquinolin-2(1H)-one (1) with (E)-5-((4-acetylphenyl)diazenyl)-2-hydroxybenzaldehyde (2) within the presence from ethanol like a solvent to give 1-((E)-2-hydroxy-5-((E)-p-tolyl diazenyl)benzylideneamino)quinolin-2(1H)-one (3). The electrophilic carbon atoms from aldehyde have be target from nucleophilic attack through amines. The final outcome from this reaction has been a compound within which the C=O double bond has replaced through a C=N double bond. This type from compound has been known through an imine (Schiff base).

3-cyanopyridines (5a-e) have been acquired through the reaction from substituted ketone through appropriate aldehydes within the presence from malononitrile while ammonium acetate [19].

![Figure 3. Synthesis of 2-amino-3-cyanopyridines (5a-e).](image)

The reaction involves first forming an imine I group that consists of the reaction of aldehyde with ammonium acetate, then the amine I group interacts with the alkylidenemalononitrile II through a condensation reaction between the two groups to give a cyclic compound III (the pyridine ring) as shown in figure 3.
Figure 4. Mechanisms of the reaction.

Table 1. Some FT-IR and $^1$H-NMR spectral data for synthesized compounds.

| Comp. No. | Characteristic bands of FT-IR spectrum (cm$^{-1}$, KBr) | $^1$H-NMR (400 MHz: DMSO-d$_6$, $\delta$, ppm, $^1$H-NMR) |
|-----------|------------------------------------------------------|------------------------------------------------------|
|           | $\nu$C=O quinolone $\nu$C= N $\nu$N=N $\nu$C-H ar. Others |                                                     |
| 1         | 1639 1597, 1452 - - 3045 $\nu$C-N 1242, $\nu$NH$_2$ 3292, 3199 | 4.2 (s,2H,NH$_2$-), 6.8-7.5(m,6H,Ar-H).               |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| **2** | - | 1570, 1472 | - | 1595 | 3040 | νC-H aliph. 2990,2920 νOH 3200, νC=O 1662, νC=O ketone 1738 |
| **3** | 1672 | 1433, 1487 | 1612 | 1595 | 3039 | νC-H aliph. 2995,2918 νC=O ketone 1738 |
| **4** | - | 1587, 1600 | - | - | 3022 | νC-H aldehyde. 2785 νC=C 750, νC=O 1701, νC=O lactone 1718. 6.65-8.14 (m,4H, Ar-H), 9.85 (s,1H, CHO). |
| **5a** | 1668 | 1560, 1483 | 1612 | 1595 | 3039,3022 | νCN 2206, νC=O lactone 1734, νNH 3350, 3438. 6.9(s,2H,NH₂), 7.2-9(m,19H,(Ar-H,HC=CH for quinolone ring and N=CH) and 11.2 (s,H,OH). |
| **5b** | 1668 | 1562, 1487 | 1608 | 1595 | 3039 | νCN 2206, νNH 3350, 3439. 6.6(s,2H,NH₂), 7-9.1(m,19H,(Ar-H,19H, (HC=CH for quinolone ring and N=CH)) and 11.2 (s,H,OH). |
| **5c** | 1668 | 1558, 1489 | 1606 | 1595 | 3035 | νCN 2206, νNH 3350, 3331. 5.6(s,2H,NH₂), 7-9.1(m,19H,(Ar-H,19H, (HC=CH for quinolone ring and N=CH)) and 10.3 (s,H,OH). |
| **5d** | 1666 | 1516, 1489 | 1610 | 1595 | 3030 | νCN 2208, νNH 3336. 4(s,3H,CH₃), 6.8(s,2H,NH₂), 7.1-9(m,18H,(Ar- |
### 3.1. Weight damage of PVC Films

Irradiation of PVC leading to diverse chemical while physical variation like a color change while, forming various fragments that have small molecular weight. As a result, irradiation from PVC with a UV light for, lengthy time leading to a deprivation within weighing, [20]. The weighing loss, percentage can give an indication of the point of PVC photodegradation. Therefore, the PVC thinlayers containing five pyridine derivatives a–e (0.5 wt %) irradiated while the weighing loss (%) was studied, utilizing based within our, previous trial of the utilize from additives, to decrease the photodegradation, of polymers [21-30], pyridine derivatives 5a–e were used at a low concentration (0.5% by weight). Also, such depressed condensation insures the compatibility of additives within the polymeric series while to avoid coloring from polymeric films. Figure 5 shows the weight loss (%) obtained due to irradiation of polymeric films. It was clear that the weight damage from the PVC films when pyridine derivatives a–e used compared with the case where no additives were used. Pyridine derivative a showed the most photostabilizing effect followed by others. Apparently, pyridine derivatives absorbed the hurtful irradiation (313 nm) that could disadvantage the PVC polymeric series [31]. Therefore, pyridine derivatives 5a–e. could be use as active photostabilizers to raise the Photostability from PVC thinlayers.

The following trend was obtained for the photostabilization effect on PVC films in presence from additives as shown below: 5a > 5b > 5c > 5d > 5e.

The outcomes clearly expose that the PVC + 5a exhibits a maximal stabilizing adequacy than other pyridine derivatives and The maximal adequacy has shown through the decrease noted within the weight loss % into the stabilized PVC samples, which indicates the lowering rates from photodegradation.
3.2. FT-IR Spectra of PVC Films

Photo-oxidation from PVC films is leading into the formation of several fragments that contains a number from efficient [32] The generality widespread fragment has the one that include a carbonyl assortion. The formation of carbonyl fragments from photo-oxidation of PVC involves forming from carbon release radical, oxidation, hydrogen free radical abstraction, elimination from hydroxyl radical followed by carbon-carbon free radical bond breaking [33]. The intensity from the carbonyl group (1726 cm\(^{-1}\)) has resembled into the intensity from a reference peak (1328 cm\(^{-1}\)) who is corresponding to the C–C bonds within the PVC polymeric chains [24] and that is done by The FT-IR spectra from the PVC (blank) thin layers before while subsequent irradiation was recorded [34]. Figure 6 clearly shows that the intensity for the C=O group was significantly increased after irradiation compared to pre-irradiation [35] Because The growth from carbonyl index shows that the being from 5a slowed rate from degradation, thus act as the most effective photo-stabilizer. The extent from degradation diminished through pyridine derivatives 5a–e content which also offers the role from pyridine derivatives 5a–e in photostabilization.

Figure 5. Change in the PVC weight upon irradiation.
Figure 6. Change within the PVC FT-IR spectra.

The PVC thinlayers were irradiated for up to 300 h and the FT-IR spectra were recorded every 50 h. The changes in the carbonyl intensity for the blank PVC was significant compared to that obtained for the PVC films containing pyridine derivatives 5a–e. Such results prove that pyridine derivatives 5a–e have a role in stabilizing the PVC polymeric materials (Figure 7).
3.3. Optical Microscopy of PVC Films

The outcomes recorded in Sections 3.1–3.2 showed that pyridine derivatives 5a–e can be utilized like additives into reduce the photodegradation from the PVC films. It was of interest to see what impact irradiation could cause to the polymeric surface. Therefore, the surface morphology was inspected by an optical microscope (400× magnifications), (Figure 8) showed Optical images (400× magnifications) from the PVC thinlayers before irradiation.
The optical images (Figure 9) from the PVC thinlayers after irradiation exhibited significantly a discoloration degree and pigment particles formation, grooves, white spots and cracks along with rough surfaces. The change was significant in blank PVC films. Whereas, such defects have been limited in non-irradiated PVC films that contain pyridine derivatives 5a–e. Such results prove the efficiency of pyridine derivatives as additives for enhancing photostabilization of PVC films with irradiated [36].

![Optical images](image.png)

**Figure 9.** Optical images (400× magnifications) from the PVC thinlayers after irradiation.

3.4. Atomic Force Microscopy (AFM) from PVC thinlayers

Images of Atomic Force Microscopy provide data for the pore sizes and surface roughness from the polymer [37]. After irradiation, the images of AFM 3D and 3D exhibited that films of PVC containing the additives (Figure 10, 11, 12, 13, 14 and 15) had fewer holes and much smoother surfaces than blank PVC films. However, Rq (roughness factor) has been additional until empty PVC films than until the thinlayers containing additives, after irradiation [38].

The rough superficies from the empty PVC thinlayer after irradiation has probably in order that bonds smashing [39] while dehydrochlorination [40]. Dehydrochlorination from PVC commonly occurs onto altitude temperatures.
Figure 10. 2D and 3D (AFM) images from PVC (empty).

Figure 11. 2D while 3D (AFM) images from PVC/a thinlayer.

Figure 12. 2D and 3D (AFM) images of PVC/b film.
Figure 13. 2D while 3D (AFM) images from PVC/c thinlayer.

Figure 14. 2D and 3D (AFM) images of PVC/d thinlayer.

Figure 15. 2D while 3D (AFM) images from PVC/e thinlayer.
Conclusions
Five 2-amino-3-cyanopyridine derivatives (5a-e) ring systems have been utilized effectively onto minimum concentrations like influential photostabilizers from poly (vinyl chloride). The additive including pyridine ring has been found into be the paramount influential. Such an additive can perform like an influential radical tie up while absorbs ultraviolet radiation, in order to the existence from a hydroxyl assortment while its altitude aromatic linked.

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