

Photostablization and Antioxidant Activity of Some New Bis(Indazole-6-Imino) Substituted-9,10-Anthracene Compounds

Abdulrahman N. Ayoob ,Ali H. Al-Mowali* and Hanan A.Al-Hazam
Department of chemistry , College of science ,University of Basrah
* E-mail of the corresponding author: ali_almowali1946@yahoo.com

Abstract

Four series of some new compounds composed from diamine and anthraquinone have been prepared and characterized by elemental analysis and spectroscopic techniques. The photostablizer activities of these compounds against low density polyethylene after exposure to Xenon U.V light were measured and compared with standard photostablizer (BHT). The antioxidant properties of these compounds were also studied using scavenger technique. Photostablization and antioxidant results for the prepared compounds indicate that these materials are very effective.

Keywords: Imino-Indazole, synthesis, photostablization, Antioxidant

1. Introduction

In the last years there has been grown interest in synthesis of Indazole derivatives due to their applications as photostablizers and antioxidants (Oliveri O. et al. 2007, Al-Amiery et al. 2012, Said M. et al. 2013 Pole E.et al. 2016, Bruce N. and Hani A. 2005). Such compounds are capable to scavenge harmful free radicals and antioxidant materials and therefore act as photostablizer and antioxidant materials. The objective of the present paper includes the synthesis of some new planar Indazole-Imino substituted anthracene and carried out detail investigation of their photostablization and antioxidant properties compared with standard materials.

2. Experimental

2.1 Materials

6-aminoindazole, anthraquinone, 1,2,5,8-tetrahydroxyanthraquinone, 1-amino-2,4-dibromoanthraquinone and 1-amino-4- hydroxyanthraquinone were obtained from Sigma aldrich in pure state. Absolute ethanol, Toluene and chloroform were obtained from Merck Company and used after being Purified according to the standard method cited in the literatures.

2.2 Instruments

CHN elemental analysis was carried out on CHNS-932-LECO apparatus. Infra-red spectra were recorded by Shimadzu 8400S as KBr disc in Wave number range (400-4000) cm⁻¹. Ultraviolet-visible were recorded by spectro Scan 80D-England spectrometer using chloroform as solvent. The ¹H NMR spectra were recorded by 500 MHz ultra shed Bruker spectrometer using DMSO as a solvent and TMS as reference. Mixer rheocord togerheometra from Hake company was used for mixing the prepared compounds with low density Polyethylene. PHI automatic compression Press was used to Press the samples of Polyethylene Xenon lamp from Bausch and Lomb which works with 150 watts was used for irradiation of polyethylene samples.

2.3 Synthesis of New Bis(Indazole-6-Imino) substituted- 9,10- Anthracene Compounds

A₁ was prepared by adding 0.01 mole of anthracene dissolved in absolute ethanol to 0.02 mole of 6-amino indazole in presence of p-toluene sulphonic acid. The mixture was refluxed for 3hours and then cooled and the solid product was collected by filtration, dried and recrystallized from toluene. The yield of yellow product, m.p. 211- 212 °C, was 70%.

A₂ was similarly prepared from reaction of 0.01 mole 1,2,5,8- tetrahydroxyanthracene-9,10-dione with 0.02 mole

of 6-amino indazole. The yield of red product, m.p. 163-165 °C was 60%.

A₃ was Prepared by the same procedure from reaction of 0.01 mole 1-amino- 2,4-dibromoanthracen- 9,10-dione with 0.02 mole of 6-amino indazole. The yield of orange product, m.p. 183-184 °C was 70%.

A₄ prepared by the same procedure from reaction of 0.01 mole 1-amino-4-hydroxyanthracene-9,10-dione with 0.02 mole 6-amino indazole. the yield of purple product, m.p. 202-203 °C, was 66%.

Table (1) shows the structures and scientific names of prepared compounds (A₁-A₄)

3.Results and Discussion

3.1 Elemental analysis

Elemental analyses of the prepared compounds are summarized in Table (2).this Table indicates that the founded percentages are in good agreement with the calculated values, which means that the reactions are successful.

3.2 Infra-red spectra

The vibration bands which were observed for compounds (A₁-A₄) are listed in Table (3). The appearance of intense band at 1635 cm⁻¹ for C=N groups and disappearance of carbonyl band at 1715 cm⁻¹ related to anthracene indicate that the reaction of anthracenes and indazoles is successful [Stuart B.2004]

3.3 Ultra violet spectra

The ultra-violet spectra of prepared compounds were characterized by three electronic transitions, the first compose of one intense band at (238- 232) nm which attributed to π→π* electronic transition. The second transition composes of two intense bands at (280-274) and (310-290) nm which attributed to charge transfer transitions.

3. 4 Proton NMR spectra

All compounds (A₁-A₄) exhibited bands with chemical shift that exists at (12-12.4) part per million related to two protons of secondary amine in addition to four bands at (5.5-7.5) part per million related to aromatic Protons. Also, the compounds exhibited signal to DMSO at (2.5) Part per million and other signal to DMSO and water at (3.5) part per million The other signals for OH, aromatic proton and NH₂ ware related to corresponding substituents in compounds A₂, A₃ and A₄ .

3.5 U.V. light stabilizers

Poly ethylene (PE) was followed by the change in the intensity of carbonyl group band absorption in Infra-red spectrophotometer before and after exposure to U.V radiation for 400 hrs. A strong absorption of carbonyl group at 1730 cm⁻¹was noticed due to the exposure to U.V light. In order to measure the strength of photostablizer activity of the prepared compounds, the PE films were mixed with (0.2, 0.4, 0.6 and 0.8) w% of the compounds after the exposure to U.V light for 400 hrs. The intensity of the absorption bands for compounds (A₁-A₄) decreases with the increasing of W% of the compounds. In order to illustrate the efficiency of Photostablizer activity of these compounds, the following relation was used [moussa K.M. et al 2007]

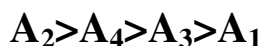
$$\Delta CO\% = \frac{T_t - T_0}{T_t} \times 100\% \quad \text{--- (1)}$$

(ΔCO%) : change of percentage of carbonyl group with time of radiation.

T_t: transmittance of carbonyl group after (t) hr of irradiation.

T₀: transmittance of carbonyl group before (t) hr of irradiation.

Figures (1-4) show the effect of weight percent of the prepared materials (A₁-A₄) as Photostablizer to PE film with irradiation time. It was found from the figures that the compound A₂ is more efficient as a photostablizer related to stander material (BHT). This is because of the presence of four OH groups which also ware capable to stablized radicals formed from degradation of PE. It was also found that the percentage 0.8% is more efficient percent for Photostablization. Although the compounds (A₁-A₄) are suitable as Photostablizers but when we compare the efficiency of (A₁-A₄) as Photostablizer to PE, figure (5) indicates that the following consequence in applied



3.6 Antioxidant Activity

The antioxidant activity of Bis(Indazole-6- Imino) substituted-9,10-anthracene compounds was evaluated against 2,2-diphenyl-1-picrylhydrazyl (DPPH) as hydrogen acceptor. DPPH absorbs visible light at 520 nanometer and therefore to test the antioxidant properties, each prepared compound (A_1 - A_4) was mixed thoroughly with DPPH and then incubated in the dark for one hour. The DPPH radical scavenging activity with ascorbic acid was also assayed for comparison. The percentage of antioxidant activity was calculated using the following equation [Venkatesan K. et al 2011]:-

$$\text{Antioxidant activity (\%)} = \frac{A_0 - A_1}{A_0} \times 100\% \quad \text{--- (2)}$$

Where A_0 is the absorbance of the control reaction and A_1 is the absorbance of the sample or standard ascorbic acid (ASC). Figure (6) shows the antioxidant activity of prepared Compounds (A_1 - A_4) together with ASC as standard reference. As shown in the figure (6), the prepared compounds (A_1 - A_4) show a pronounced antioxidant activity compared to that of (BHT). Compound (A_2) has greater antioxidant activity and this may be attributed to the presence of four OH groups in addition to NH groups. Figure (6) also shows the sequence of antioxidant activity as follows:-

$$A_2 > A_4 > A_3 > A_1$$

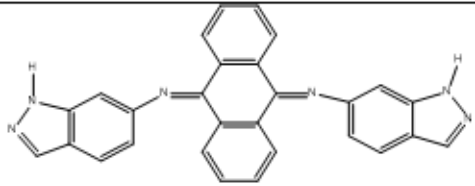
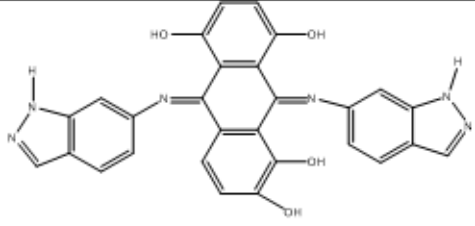
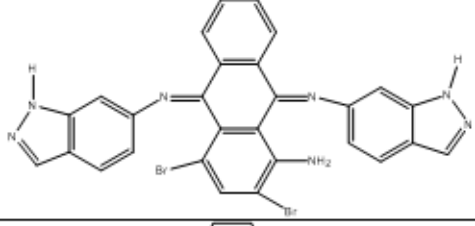
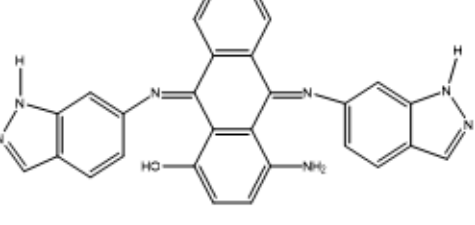
4. Conclusion

The present study demonstrated that the new Bis(Indazole-6- Imino substituted-9,10- anthracene) exhibited feasible photostabilizer and antioxidant properties.

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Table (1) structures and scientific names of compounds (A₁-A₄)

<i>Symbol</i>	<i>Scientific name</i>	<i>Structure</i>
<i>A₁</i>	9,10-di((1H-indazol-6-yl)imino)anthracene	
<i>A₂</i>	9,10-bis((1H-indazol-6-yl)imino)-9,10-dihydroanthracene-1,2,5,8-tetraol	
<i>A₃</i>	9,10-bis((1H-indazol-6-yl)imino)-2,4-dibromo-9,10-dihydroanthracen-1-amine	
<i>A₄</i>	9,10-bis((1H-indazol-6-yl)imino)-4-amino-9,10-dihydroanthracen-1-ol	

Tablet (2) Element Analysis of compounds (A₁-A₄)

<i>Symbol</i>	<i>Molecular formula</i>	<i>Theoretical %C (Founded)</i>	<i>Theoretical %H (Founded)</i>	<i>Theoretical %N (Founded)</i>
<i>A₁</i>	C ₂₈ H ₁₈ N ₆	76.70 (76.63)	4.14 (4.09)	19.17 (19.11)
<i>A₂</i>	C ₂₈ H ₁₈ N ₆ O ₄	66.93 (66.90)	3.61 (3.57)	16.73 (16.70)
<i>A₃</i>	C ₂₈ H ₁₇ Br ₂ N ₇	55.02 (55.08)	2.80 (3.0)	16.04 16.0
<i>A₄</i>	C ₂₈ H ₁₉ N ₇ O	71.63 (71.6)	4.08 (4.04)	20.88 (20.85)

Table (3) the most importation vibrational wave number of functional groups in compounds (A₁-A₄)

Symbol	N-H	C=N	C=C Ring str.	C-H Aromatic str.	C-H Aromatic bending	O-H	-NH ₂	C-Br
A ₁	3356.1	1635.6	1400- 1582	3147- 3201	948.9	-	-	-
A ₂	3356.1	1635.6	1400- 1582	3147- 3201	948.9	3510	-	-
A ₃	3352.2	1635.6	1400- 1582	3147- 3201	948.9	-	3442	740
A ₄	3356.1	1635.6	1400- 1582	3147- 3201	948.9	3595	3445	-

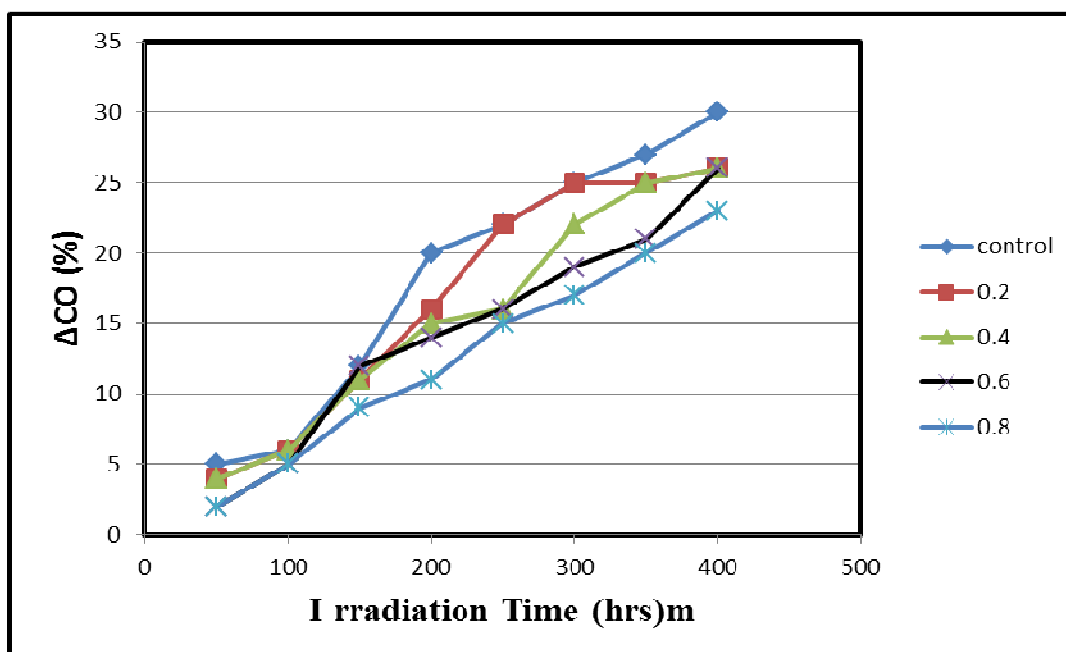


Figure (1): relation between (Δ CO%) and irradiation time of PE containing the compound A₁

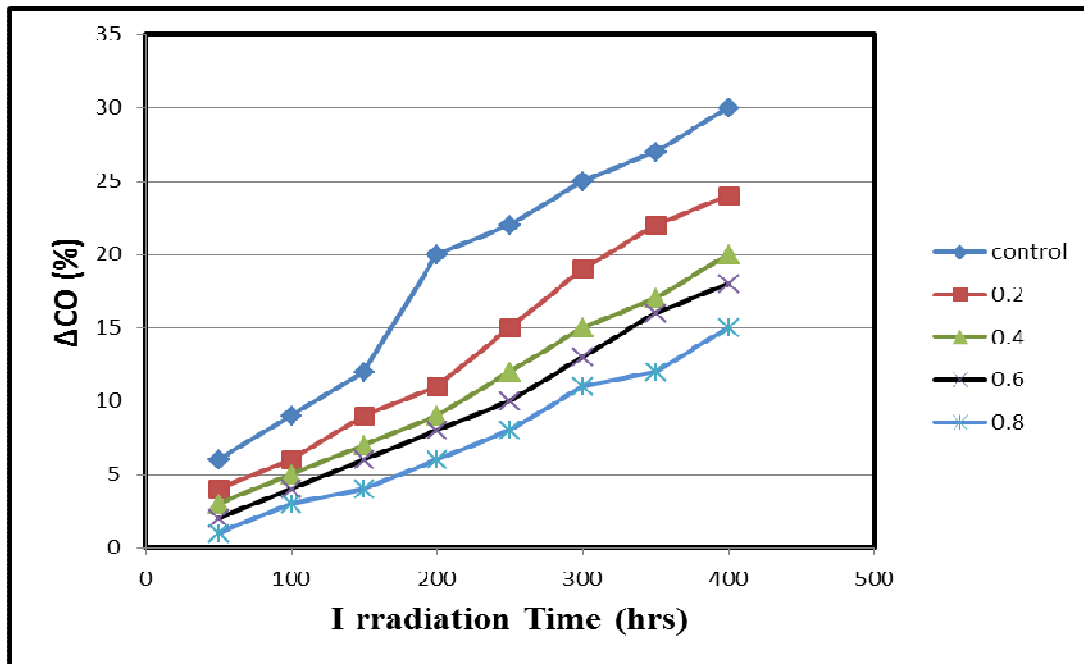


Figure (2): relation between ($\Delta CO\%$) and irradiation time of PE containing the compound A_2

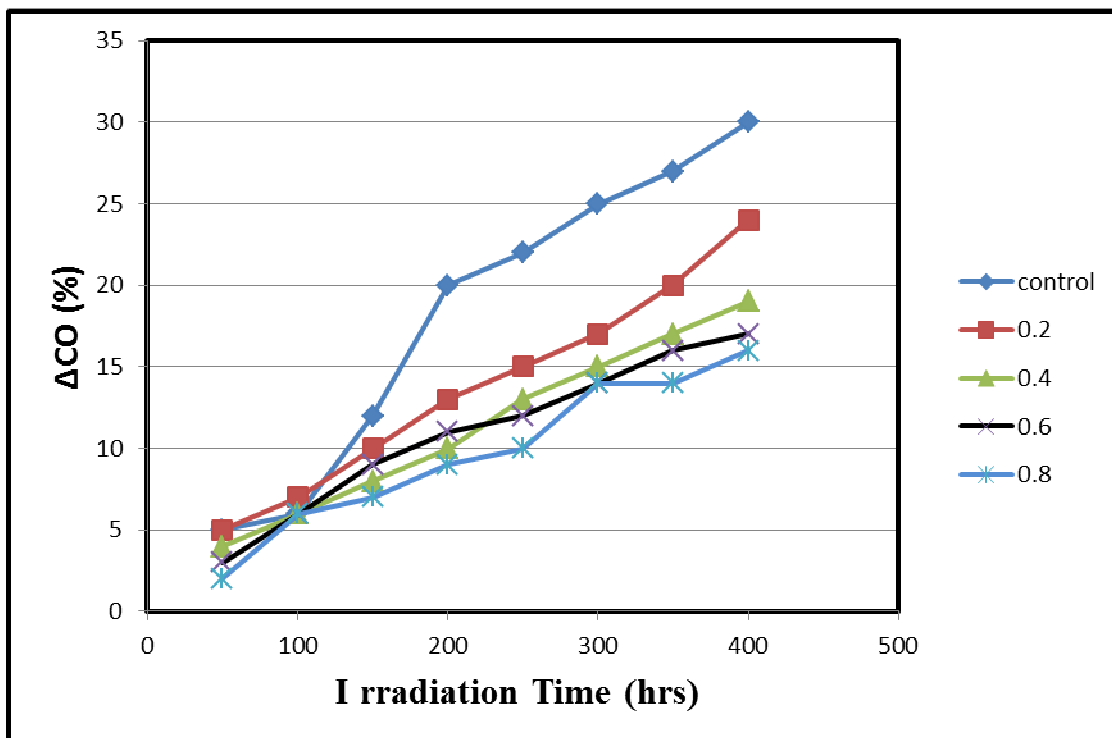


Figure (3): relation between ($\Delta CO\%$) and irradiation time of PE containing the compound A_3

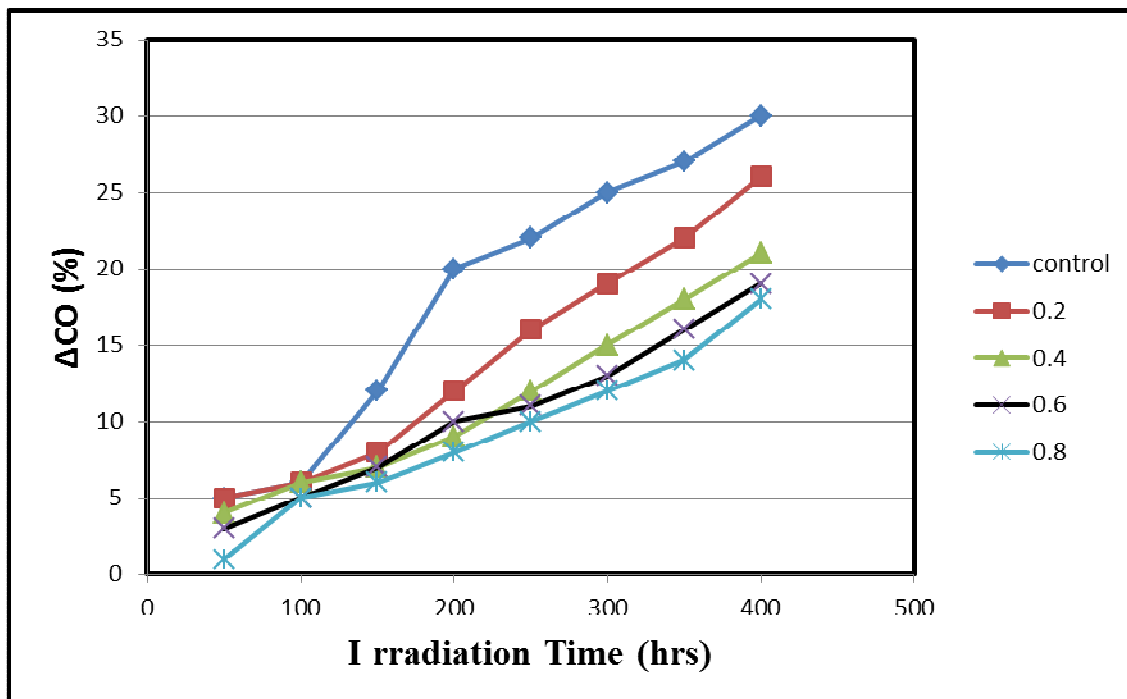


Figure (4): relation between ($\Delta CO\%$) and irradiation time of PE containing the compound A_4

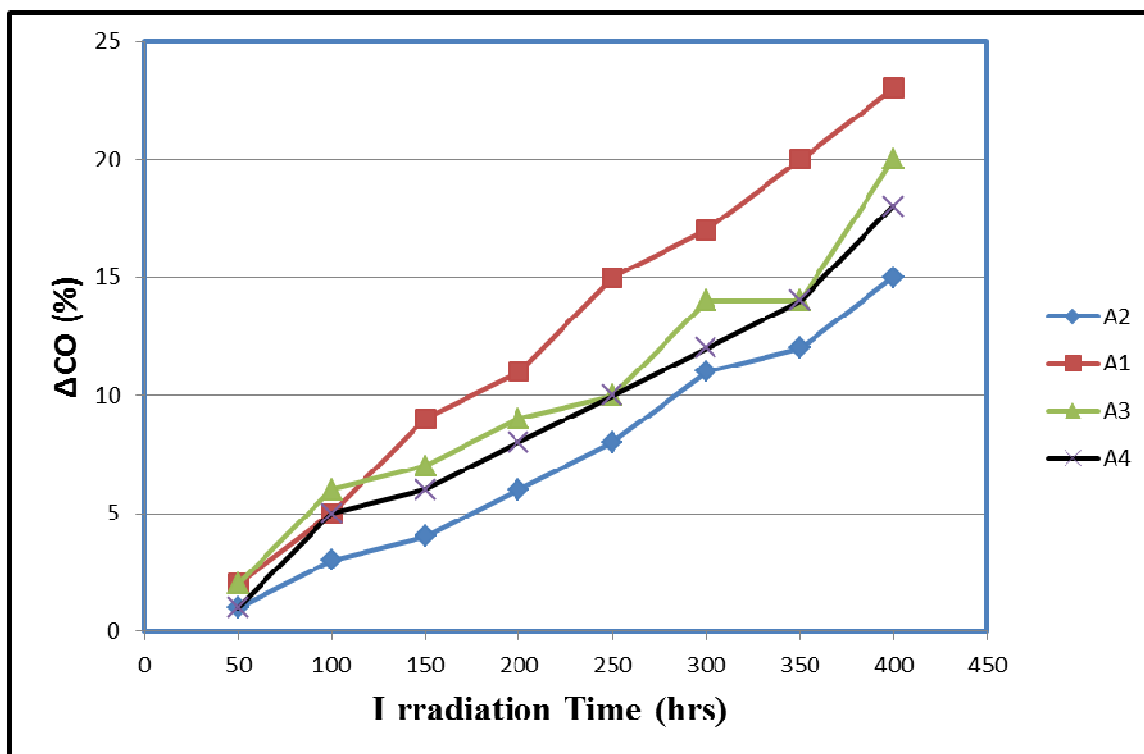


Figure (5): relation between ($\Delta CO\%$) with irradiation time of PE containing the efficient weight of the additives

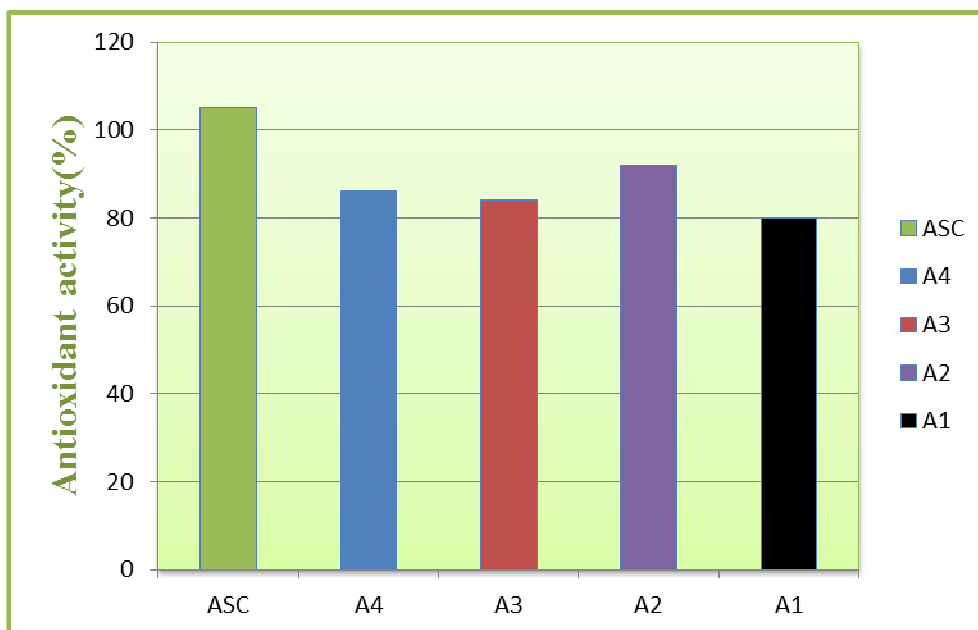


Figure (6) Antioxidant properties of (A₁-A₄) compounds