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Synthesis and Characterization of Some Dimmer Schiff base and Study Activity as Photo stabilizer for Low Density Polyethylene.

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ABSTRACT

Six new compounds from α,ω - bis (p-R-aniline benzilidene-4-oxy) Octamethane; where R = H, Cl, Br, Me, OMe and NO₂ have been prepared and characterized by CHN elemental analysis, UV, ¹H-NMR and IR. The geometrical optimization for the above dimmer compounds were carried out in order to find out the most stable stereo chemical by using PM3 method. The photo chemical efficiency of prepared dimmer compound for low density polyethylene as compared with standard photo stabilizer (BHT) was carried out as show in scheme 1.

Keywords: α,ω - bis (p-R-aniline benzilidene-4-oxy) Octamethane , dimmer compounds , photo stabilizer

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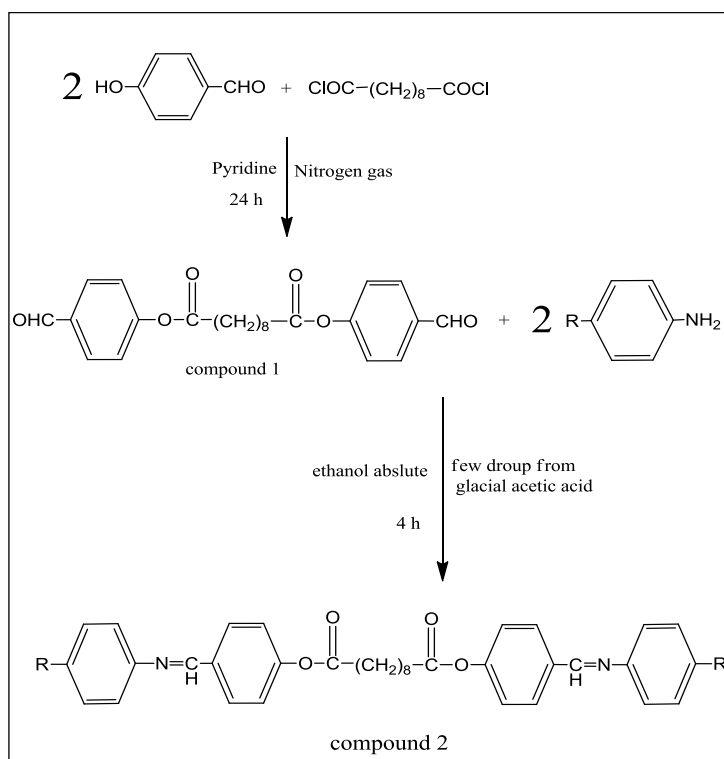
INTRODUCTION

It is well known that virtually all commercial organic polymers including elastomers, thermoplastic, synthetic fiber and adhesive have to be stabilized against the harmful effect of sunlight and oxygen. For that we can use many of stabilizers against UV and oxygen to prevent the polymers [1-2]. In current studies, many researchers were trying to prepare UV stabilizers that have high weight and compatibility with polymers [3-5]. Polymer oxidation degradation can be followed using infrared spectroscopic techniques using that rate of formation of carbonyl group at $1700 - 1800 \text{ cm}^{-1}$ [6-8]. Difference in the relative heights of absorption bands or existence ability of these compounds as stabilizers.

Shiff bases compounds were very important materials that interfere in a wide field of chemistry [9-15], they also act as intermediates for the preparation of many compounds that have a variety of biological activity [16-20].

In the present work, we prepared some new longitudinal dimer shiff bases that derived from α,ω -bis (4-formyl phenyl-1,4-oxy) Octamethane. These dimers were characterized by CHN, IR and $^1\text{H NMR}$. Photochemical efficiency of the dimer shiff bases has been studied theoretically by semi-empirical molecular orbital theory at the level of PM3 theory to show the approach, interference and agglutination between dimer compounds and low density polyethylene.

The aim of the study, synthesis, characterization, theoretical and photo stability studies for this compound [α,ω - bis (p-x-aniline benzilidene-4-oxy)] Octamethane derivatives Scheme 1.



Scheme 1
EXPERIMENTAL

Preparation of compound (1) : ω,α - bis (4-formyl phenyl-4-oxy) Octamethane[21]

p-hydroxy benzaldehyde (0.08 mole) in (30 ml) of dry pyridine was added with the sebacoyl chloride (0.04 mol) in (5 ml) of dry pyridine was stirred at room temperature under nitrogen atmosphere overnight. The solid product was filtered off and wash with distilled water then dried. The crude product was recrystallized from absolute ethanol; the product was white precipitate (yeild 85%, melting point 60°C).

Preparation of compound (2) : α,ω - bis (P-substituted- aniline benzilidene-4-oxy) Octamethane [22]

4-substituted aniline (0.084 mole) was added to a hot solution of compound (1) (0.04 mole) in absolute ethanol (30 ml) in a (50 ml) conical flask fitted with calcium chloride guard tube and added a few droup from glacial acetic acid to solution, while cooling to room temperature, the mixture was stirred for 4hs. White precipitate formed which was filtered off and recrystallized from absolute ethanol to give crystals which was dried in vacuom at 30°C. Melting point and yeild of product show in Table 1.

Table 1: Melting point and yield for all compounds

Substituent	Melting Point °C	%Yield
H	148	80
Cl	155	86
Br	160	85
CH ₃	160	90
OCH ₃	120	90
NO ₂	180	88

Physical Measurements

IR spectra as KBr discs in the range (200-4000) cm⁻¹ were recorded on a Pye-Unicam SP3-300s IR spectrometer. Electronic spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer in DMSO solution. ¹HNMR spectra in DMSO-d₆ were recorded on Joel EX-90 FT using TMS as an internal standard. Melting point was measured on Gallenkamp melting point apparatus and is uncorrected. The carbon hydrogen and nitrogen analyses were carried out with Perkin-Elmer240M elemental analyzer.

Theoretical Calculations

Theoretical computations were performed in a Pentium IV PC. Semi-empirical self-consistent field molecular orbital (SCF-MO) method at PM3 level [23] within the restricted Hartree-Fock (RHF) [24] formalism has been considered. Geometry optimization is carried out

by using a conjugate gradient method (Polak–Ribiere algorithm) [25]. The SCF convergency is set to 0.001 kcal mol⁻¹, while the RMS gradient is set to 0.001 kcal/(Å mol) in the calculations.

RESULTS AND DISCUSSION

The structure of dimmer compounds are charatrized by CHN, IR, UV and ¹H-NMR . The elemental analyses are in good agreement with calculated values as show in Table 2.

Table 2: Elemental analyses for all compounds

Substituent	Calculated			Found		
	%C	%H	%N	%C	%H	%N
H	77.14	6.43	5,00	77.17	6.48	5.04
Cl	68.68	5.40	4.45	68.65	5.41	4.41
Br	60.16	4.73	3.98	60.11	4.72	3.85
CH ₃	77.81	6.82	4.77	77.86	6.85	4.74
OCH ₃	72.38	6.34	4.44	72.45	6.35	4.62
NO ₂	66.46	5.23	8,61	66.50	5.28	8.66

IR spectra

The IR spectra of the new synthesis compounds were measured in the region between 200-4000 cm⁻¹ depend on literatures[26-28] . Their spectra showed the two strong absorption band at 1749-1741 cm⁻¹ for C=O vibration stretching and at 1627 – 1620cm⁻¹ for C=N vibration stretching . The spectra showed also medium band between 1598-1581 cm due to C=C stretching which are characteristic aromatic rings . furthermore , the spectra showed stretching vibration bands between 2927 -2842 cm⁻¹ attributed to C-H Aliphatic while the strong absorption bands between 1294 – 1161 cm⁻¹ attributed to C-O-C group. The most important bands of their compounds are shown in Table 3

Table 3 . IR spectra data of the dimmer compounds

Sub	C-H (str.) Alphatic (w)	C-H (str.) Aromatic (w)	C=O ester (s)	C=N azomethane (s)	C=C Armoatic (w)	C-O-C ether (s)
H	2927-2852	3043	1742	1627	1581	1159, 1264
Cl	2927-2852	3039	1741	1620	1591	1164, 1288
Br	2924-2842	3034	1741	1623	1581	1162, 1284
CH ₃	2925-2862	3036	1748	1625	1598	1163, 1294
OCH ₃	2925-2852	3035	1747	1627	1581	1171, 1294
NO ₂	2927-2872	3053	1749	1625	1583	1161, 1292

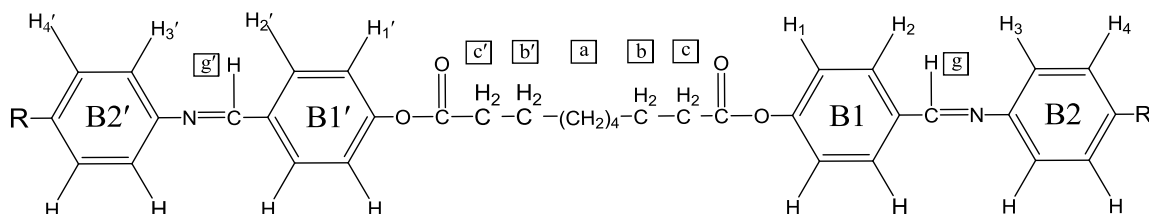
UV (Ultraviolet) spectra

The UV spectra of the dimmer compounds were measured at concentration of 1×10⁻⁴ molar using dichloromethane CH₂Cl₂ as a solvent. The spectra showed two bands; the first at nearly 265 nm related to electronic transition for azomethane and aromatic ring with shiff base that

connected with carbon atom pH_C, while the second band at 320 nm as a result from electronic transition for azomethane that connected with shiff base from nitrogen pH_N[29-30].

¹H-NMR spectra

The dimmer compounds are represented in Scheme 2



Scheme 2

All the spectra showed a signal peak at 5.32 ppm due to CH₂Cl₂ solvent. protons (a) appeared as a signal band at 1.35 – 1.21 ppm related to aliphatic, while protons (b) at 1.98 – 1.75 ppm as a multiplet peaks due to attractive between protons (b) with protons (a) and (c). Protons (c) appeared at 2.65 – 2.31 ppm as a triplet. Protons (g) appeared at 8.94 – 8.55 ppm as a single. The aromatic region ; B1 and B2; appeared as AX system due $\Delta\nu/J > 10$ [31].

Table 4: The values of chemical shift(ppm) and coupling constant (Hz)

Sub R-	Aliphatic Protons					Aromatic Protons			
	CH ₂ (a)	CH ₂ (b)	CH ₂ (c)	H(g)	Sub	H ₁ ,H ₁ '	H ₂ ,H ₂ '	H ₃ ,H ₃ '	H ₄ ,H ₄ '
H	1.317 s	1.841 m	2.630 t J=8.7	8.717 s	m	7.035 d J=7.8	7.567 d J=7.8	m	m
Cl	1.241 s	1.843 m	2.641 t J=8.7	8.942 s	-	6.938 d J=7.8	7.557 d J=7.8	7.867 d J=6.9	8.418 d J=6.9
Br	1.324 s	1.807 m	2.433 t J=7.8	8.761 s	-	7.108 d J=7.2	7.419 d J=7.2	7.891 d J=7.5	8.416 d J=7.5
CH ₃	1.352 s	1.943 m	2.618 t J=8.1	8.553 s	CH ₃ 2.225 s	7.053 d J=7.2	7.418 d J=7.2	7.793 d J=6.9	8.367 d J=6.9
OCH ₃	1.271 s	1.832 m	2.344 t J=8.1	8.687 s	OCH ₃ 3.651 s	6.983 d J=7.2	7.436 d J=7.2	7.820 d J=6.9	8.247 d J=6.9
NO ₂	1.213 s	1.853 m	2.350 t J=8.7	8.753 s	-	7.027 d J=7.5	7.450 d J=7.5	7.825 d J=7.2	8.464 d J=7.2

s = singlet , d = doublet , t = triplet , m = multiplet

Photochemical Efficiency

The measurement was performed by mixing each dimmer with low density poly ethylene with different percentages weight and the designed as thin film templates with thickness 1mm [32]. The templates were exposed to altar violet radiation by using xenon lamp for different time (50 ,100 ,150 , 200 ,250 , 300) hrs[33]. The change of the carbonyl

absorption due to photo degradation of the polymers was followed by using infrared spectroscopy. The results of measurement show the efficiency of each prepared dimmer shift base in photo stabilizing the low density poly ethylene Fig .1.

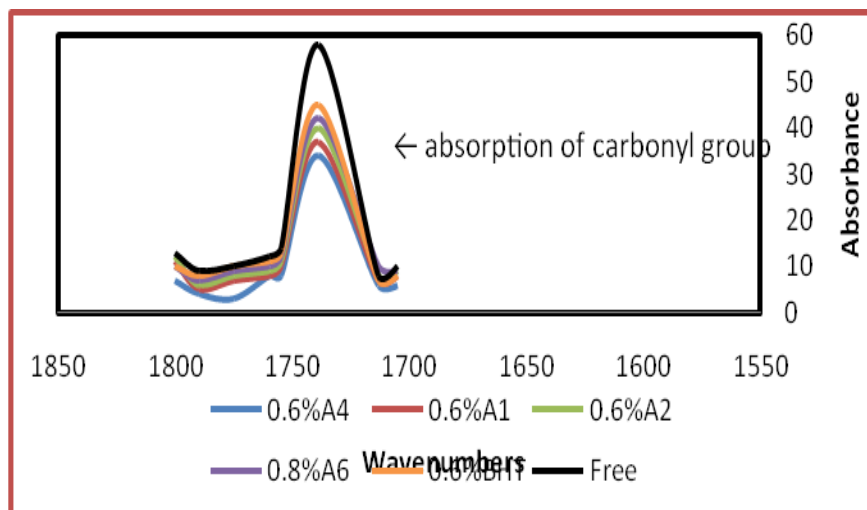


Figure 1: IR Spectra absorption for poly ethylene carbonyl after 300 hrs. with different percentage of prepared compounds

The semiempirical method PM3 results show the high efficiency of dimmer compounds characterized by almost linear structure which enhances them to approach interfere and agglutinate with polymer as show in Fig.2-3.

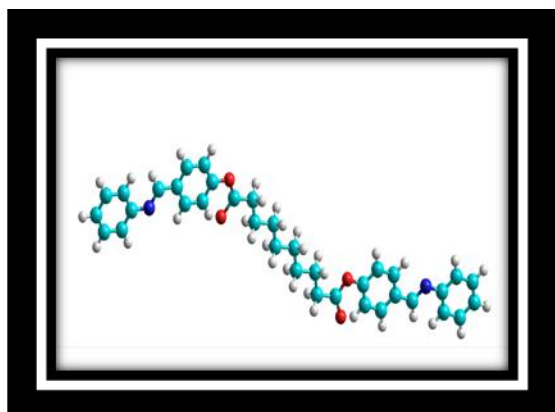


Figure 2: The stereo chemistry of compound A1

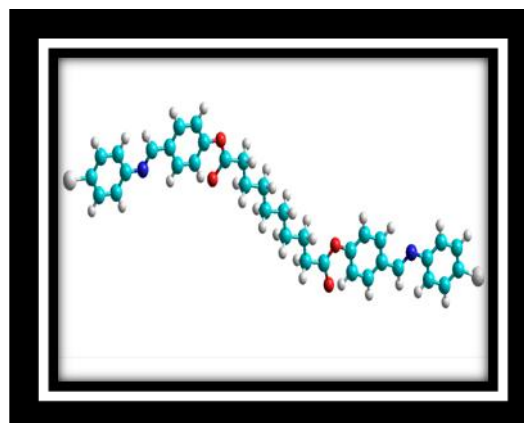


Figure 3: The stereo chemistry of compound A2

And this facilitates scavenging of hydrogen from dimeric compound by generating free radical from irradiated polymer.

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