

# Synthesis, Characterization of some New 4-Thiazolidinone of Acenaphthoquinone

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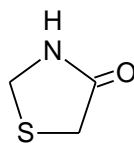
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**Abstract**— This work summarized with Synthesis of schiff's bases 1(a-c) from reaction of parent compound acenaphthoquinone with primary amines . Treating of imines compounds with thioglycolic acid was produced thiazolidinone derivatives 2 (a-c) .The structures of synthesized compounds were confirmed by using some spectroscopic analysis such as FT.IR , <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral

**Keywords**— thioglycolic acid ; <sup>13</sup>C-NMR spectra ; Acenaphthenquinone; thiazolidin

## I. INTRODUCTION

Thiazolidinone-4-one are the derivatives of thiazolidine which belong to an important group of heterocyclic compounds containing sulfur and nitrogen in a five member ring <sup>(1)</sup> 1,3-Thiazolidin-4-ones are heterocyclic at position 1 containing a sulfur atom , position 3 nitrogen and position 4 carbonyl group <sup>(2)</sup> figure (1) .Thiazolidine and its composites are key components of many natural products and drugs . In addition, Thiazolidine found to uses as antitubercular <sup>(3)</sup>, antibacterial <sup>(4)</sup>, anti-inflammatory <sup>(5)</sup> , as antiviral agents, especially as anti-HIV agents <sup>(6)</sup>, anticancer <sup>(7,8)</sup>, anticonvulsant <sup>(9)</sup> and antidiabetic activity <sup>(10)</sup>.



Figure(1): Thiazolidinone ring

## II. EXPERIMENTAL PART

### A. General procedure for the preparation of imines 1(a-c)

In general<sup>(11)</sup>, imines prepared by mixed the amine with acenaphthoquinone in (25 ml) of Suitable solvent ethanol and add (10 -15) drops of glacial acetic acid were refluxed in water bath for ( 24 – 25) h .The reaction was followed up with TLC the eluent using [Hexane :Ethyl acetate (7:3 )]. When the reaction completion the solvent removed by evaporation then the product recrystallized by methanol.

### B. (1Z,2E)-N,N'-bis(4-methylphenyl)-2a,5-dihydroacenaphthylene-1,2-diimine (1a)

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with 4-methylaniline (1.176 g , 10.978 mmol) m.p = 220-222 R<sub>f</sub> = 0.9 IR (KBr disk):( 1629. 85) cm<sup>-1</sup> (C=N) yield = 78% .

### C. (1Z,2E)-N,N'-bis(4-(dimethylamino) phenyl)-2a,5-dihydro acenaphthylene-1,2-diimine (1b )

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with N,N-dimethylbenzene-1,4-diamine (1.495 g , 10.978 mmol) m.p = 246-248 R<sub>f</sub> = 0.7 IR (KBr disk): (C=N) 1654. 92 cm<sup>-1</sup> yield = 76 % .

### D. (2Z)-2-[4-bromophenylimino]-6,8a-dihydroacenaphthylene-1(2H)-one (1c)

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with 4- bromoaniline (0.94g , 5.489 mmol) m.p = 238-240 R<sub>f</sub> = 0.8 IR (KBr disk): 1654. 92cm<sup>-1</sup> (C=N) yield = 72 % .

### E. General Procedure of thiazolidinones 2(a-c)

In general, <sup>(12)</sup> the thiazolidinones were mixed with imines 1(a-c) and thioglycolic acid in (15 ml) chloroform , Then refluxed for (18-24) h with Stirring. The reaction monitored by TLC using eluent [n-Hexane-Ethyl acetate (3:7) ] . When The reaction completed the solvent removed to give thiazolidinone. The product was precipitated and recrystallized with the addition of methanol droplets.

### F. N-(4-methylphenyl)-4'-spiro[acenaphthylene-2,2'-thiazolidine] (2a)

Prepared by reacting (1g, 2.778 mmole) (2E)-2-[4-methylphenyl] imino]-1,2-diphenyl ethanone (1a) and (0.674mL, 0.447g, 5. 556 mmole) of thioglycolic acid. R<sub>f</sub> = 0.7 , yield = 63 % , m.p. =232-234 °C. IR (KBr disk): 1689.64 cm<sup>-1</sup> (-N-C=O).

G. *N*-(4--(dimethylamino) phenyl)-4'-spiro[acenaphthylene-2,2'-thiazolidine] (2b)

Prepared by reacting (1g, 3.049 mmole) (1*Z*,2*E*)-*N*,*N*'-bis (4-(dimethylamino) phenyl)-2*a*,5-dihydroacenaphthylene-1,2-diimine(1b) and (0.354 mL, 0.469 g, 6.098 mmole) of thioglycolic acid.  $R_f = 0.7$ , yield = 60%, m.p. = 255-257°C. IR (KBr disk): 1686.51 cm<sup>-1</sup> (-N-C=O)

H. *N*-(4-bromophenyl)-4'-spiro[acenaphthylene-2-thiazolidine] (2c)

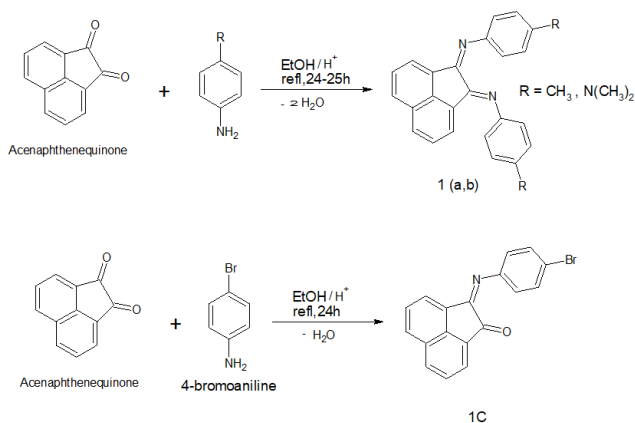
prepared by reacting (1g, 2.974 mmole) (2*Z*)-2-[(4-bromophenyl)imino]-6,8*a*-dihydroacenaphthylene-1(2*H*)-one (1c) and (0.361 mL, 0.272 g, 2.974 mmole) of thioglycolic acid  $R_f = 0.8$ , yield = 62%, m.p. = 236-238 °C. IR (KBr disk): 1698.85 cm<sup>-1</sup> (-N-C=O)

### III. MEASUREMENTS

Melting points were determined in open capillary tubes using an electro thermal melting point /SMP31 apparatus. FTIR spectra in the range (200-4000) cm<sup>-1</sup> were recorded as KBr discs using a Shimadzu FTIR spectrophotometer. The <sup>1</sup>H-NMR were recorded on VARIAN spectrophotometer (300 MHz), the <sup>13</sup>C-NMR spectra were recorded using VARIAN spectrophotometer (75 MHz) relative to the internal standard tetramethylsilane (TMS), DMSO-d<sub>6</sub> used as solvent.

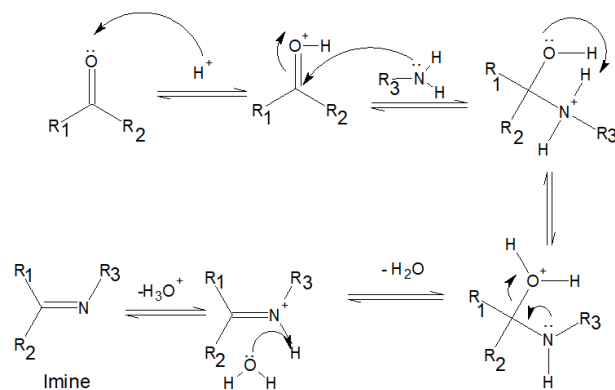
### IV. RESULT AND DISCUSSION

Prepared Compounds 1(a-c) from the reaction of acenaphthoquinone with 4-methylaniline, *N,N*-dimethylbenzene-1,4-diamine and 4-bromoaniline respectively with the presence of glacial acetic acid in absolute ethanol as shown in scheme (1).



scheme (1): Synthesis of the compounds 1(a-c)

The reaction involves a nucleophilic attack of the amine group on the carbon of the carbonyl group of the ketone to form a compound *N*-(substituted hemiaminals) which loses a water molecule to give the stable compound. Mechanism of imines formation<sup>(13)</sup> shown in scheme (2)



scheme(2): Mechanism of imines formation

Measured the melting points Compounds 1(a-c) as shown in Table (1) diagnosed by specifying (FT-IR) shown in Table (2). It features ranges corresponding to the expansion vibrations, azomethine band (C=N), aromatic (C=C), bands aromatic (C-H) and aliphatic (C-H). These bands occur (1629.85, 1654.92, 1654.92), (1587.42, 1602.85, 1598.99), (3051.39, 3047.53, 3055.24), (2916.37, ---, 2835.36) cm<sup>-1</sup> respectively.

Table (1) shows the physical properties data imines 1(a-c)

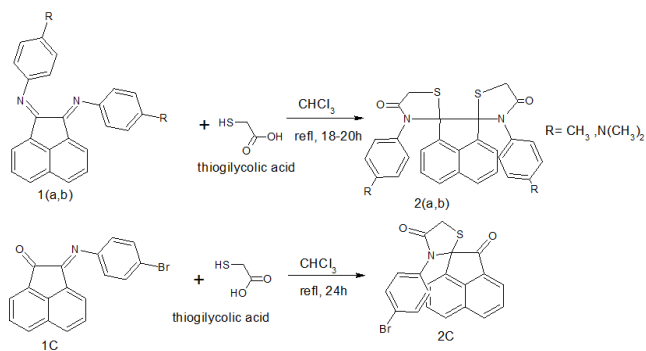
Comp. 1 (a-c)	m.p. °C	Colour	Reaction time
1 a	220-222	Orange	24h
1b	246-248	Red	25h
1c	238-240	Yellow	24h

Table (2): shows IR spectra of Imines 1(a-c)

Comp. 1(a-c)	Aromatic C-H stretching cm <sup>-1</sup>	Aliphatic C-H stretching cm <sup>-1</sup>	Azomethine C=N stretching cm <sup>-1</sup>	Aromatic C=C stretching cm <sup>-1</sup>
1 a	3051.39	2916.37	1629.85	1587.42
1b	3047.53	2875.86	1654.92	1602.85
1c	3055.24	2972.31	1654.92	1598.99

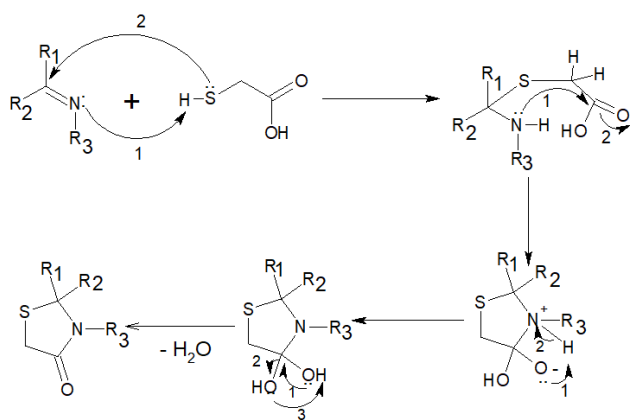
### V. SYNTHESIS 4-THIAZOLIDINON

Compounds were 2(a-c) prepared from the reaction of imines 1(a-c) with acid thioglycolic acid in absolute chloroform as shown in scheme (3).



Scheme (3): Synthesis of the compounds 2(a-c)

Involved mechanism cycloaddition<sup>(13)</sup> formation 4-Thiazolidinone as shown in Scheme (4)



scheme (4) Mechanism of 4-Thiazolidinone formation

The melting point of the prepared compounds 2(a-c) was measured as shown in Table (3) The (FTIR) spectra Table (4) of compound 2(a-c) show featured packages most notably, C-H aromatic, aromatic C=C, aliphatic C-H and carbonyl amide group which occur within; - (3051.39, 3054.83, 3069.35), (1608.63, 1606.28, 1691.57), (2920.23, 2984.09, 1600.77), (1689.64, 1686.51, 1600.77)

Table 3: physical properties of thiazolidinones 2(a-c)

Comp. 2 (a-c)	m.p. °C	Colour	Reaction time
2 a	232-234	Grey	24h
2b	255-257	Yellow	25h
2c	236-238	White	24h

Table (4): FTIR spectral data of Thiazolidinones 2(a-c)

Comp. 2 (a-c)	Aromatic C-H stretching $\text{g cm}^{-1}$	Aromatic C=C stretching $\text{cm}^{-1}$	Aliphatic C-H stretching $\text{g cm}^{-1}$	Amide C=O stretching $\text{cm}^{-1}$ (thia-)
2 a	3051.39	1608.63	2920.23	1689.64
2b	3054.83	1606.28	2984.09	1686.51
2c	3069.35	1691.57	1600.77	1698.58

The <sup>1</sup>H-NMR of 2(a-c) shows signals at  $\delta$ (2.39) ppm for CH<sub>3</sub> Component (2a) and  $\delta$ (2.51) ppm for N-(CH<sub>3</sub>)<sub>2</sub> Component (2b) also show characteristic chemical shift (CH<sub>2</sub>) group of thiazolidinone ring showed doublet of doublet signal at chemical shift  $\delta$  [dd-(4.10- 4.05ppm,  $J=15\text{Hz}$ ) - (4.08- 4.03ppm,  $J=15\text{Hz}$ ) - (4.12- 4.07ppm,  $J=15\text{Hz}$ ), and doublet of doublet signal at chemical shift  $\delta$  [dd-(4.34- 4.29ppm,  $J=15\text{Hz}$ ) - (4.23- 4.18ppm,  $J=15\text{Hz}$ ) - (4.27- 4.22ppm,  $J=15\text{Hz}$ ) respectively. a multiplet signal at  $\delta$  (6.72-8.01), (6.39-8.29), (6.89-8.28) ppm for aromatic protons respectively as show Table (5).

<sup>13</sup>C-NMR spectral of 2(a-c) gives signal at  $\delta$ (20.89) ppm for carbon -CH<sub>3</sub> Component (2a), at  $\delta$ (40.11) ppm for carbon -NCH<sub>3</sub> Component (2b) and characteristic signal of 2(a-c) of thiazolidinone ring show at [ (33.17), (32.92), (33.07) ppm] for carbon -CH<sub>2</sub>-, at [ (72.98), (73.55), (73.29) ppm] for carbon S-C-N, at [ (172.67), (172.55), (172.41) ppm] for carbon -N-C=O as show Table (6).

Table(5): <sup>1</sup>H-NMR spectral data of Thiazolidinones 2(a-c)

Comp. 2 (a-c)	thiazolidin-4-one ring		Aromatic proton	Aliphatic proton
	C-H ring, $J$ Hz	C-H ring, $J$ Hz		
2 a	4.10-4.05 ppm $J=15\text{Hz}$	4.34-4.29ppm $J=15\text{Hz}$	6.72-8.01	2.39
2b	4.08-4.03 ppm $J=15\text{Hz}$	4.23-4.18ppm $J=15\text{Hz}$	6.39-8.29	2.51
2c	4.12-4.07ppm $J=15\text{Hz}$	4.27-4.22ppm $J=15\text{Hz}$	6.89-8.28	----

Table(6) <sup>13</sup>C-NMR spectral data of Thiazolidinones 2(a-c)

Comp. 2 (a-c)	Chemical shift ppm				
	-CH <sub>2</sub> -	C-N-S	N-C=O	C-Ar	Other
2 a	33.17	72.98	172.67	118.08 - 148.24	-(CH <sub>3</sub> ) 20.89
2b	32.92	73.55	172.55	112.37-150.05	-----
2c	33.07	73.29	172.42	121.72-140.58	-(NCH) 40.11

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