Sun Light Degradation of α-Naphtholbenzein Using TiO_2 as a Catalyst

Ahmed Khadem Abass
Chemistry department - College of Science - University of Al Qadisiya

الخلاصة

تم دراسة تفاعل التحلل الضوئي لـ α- نفثول بنزين مع TiO_2 كعامل مساعد ضوئي باستخدام ضوء الشمس . وتم تعيين تأثير العوامل المختلفة مثل: زمن التشعيع وتفاعلات الضوء والظلام ووزن TiO_2 وتراكيز H_2O_2 والاوكزالات. وضحت التجارب بان التحلل الضوئي يكتمل عند الزمن ٢.٣٠ ساعة وان وجود TiO_2 و O_2 كان عاملا مهما لزيادة سرعة التفاعل في الضوء والظلام. وكان الوزن الأمثل للعامل المساعد هو ٠.٤ غم حيث كان ثابت السرعة ١٩×$^{-2}$١٠$^{-٢}$ ساعة$^{-١}$. وان سرعة التفاعل تزداد بزيادة تركيز الـ H_2O_2 حتى ١٢ مليمول . كذلك بينت التجارب بان سرعة التحلل الضوئي تزداد بزيادة تركيز ايون الاوكزالات. وبينت حركية التفاعل بان التفاعل من المرتبة الأولى الكاذبة.

Abstract

The photolysis of α-naphtholbenzein with TiO_2 as photo catalyst has been investigated using solar light. The effect of various parameters such as: time of irradiation, light and dark reactions, TiO_2 loading, H_2O_2 and oxalate concentrations have been determined. The experiments explained that the photolysis was completed at 2.5 hr. In both light and dark reactions, the presence of TiO_2 and O_2 was an important factor to increase the rate of reaction. The optimum loading of the catalyst was 0.4g in which the rate constant was 19×10^{-2} hr^{-1}.The rate of reaction increased with increasing the millimoles of H_2O_2 until 12 millimoles. Also the experiments showed that the photolysis rate was increased with increasing the concentration of oxalate ion .The kinetics of reaction explained that the reaction was from pseudo first order.

Key words: *α-naphtholbenzein, photolysis,* TiO_2.

Introduction

Solar radiation is regarded of interest being the existence of ultraviolet radiation the key of some homogeneous and heterogeneous photocatalytic Processes, such as TiO_2/UV and H_2O_2/Fe^{+2}/UV-Vis or H_2O_2 /Fe^{+3}/ UV-Vis. system (Photo-Fenton) [1-3]. Heterogeneous photocatalytic process includes the use of UV radiation to Photoexcite semiconductor catalyst in the presence of oxygen. Under these conditions, oxidizing components-bound hydroxyl radical or free holes are generated [4]. The photocatalyst titanium dioxide (TiO_2) is a wide band gap Semiconductor (3.2ev) and it is used as a photocatalyst for the treatment of organic [5-8] and dye pollutants [9-15].

TiO_2 is regarded as the best photo catalyst due to high stability, good performance and low cost [16)] .In TiO_2/UV light system, a titanium Peroxide semiconductor absorbs UV light and generates hydroxyl radicals. During UV illumination of TiO_2, conduction band electrons and valence band holes are initially yielded (equation 1). Band electrons interact with surface adsorbed molecules oxygen to yield super oxide radical anions (equation 2), while band holes interact with water to produce hydroxyl radical (equation 3) [17].

$$\mathbf{TiO_2 + hv \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad \ldots\ldots\ldots\ldots\ldots (1)}$$

$$\mathbf{e^{-}_{cb} + O_2 \rightarrow O^{\cdot -}_{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)}$$

$$\mathbf{h_{vb}^{+} + 1/2H_2O \rightarrow H^{+} + 1/2O_2 \ldots\ldots\ldots\ldots\ldots\ldots (3)}$$

The photo catalysis processes that take place on the TiO2 -semiconductor can be represented by **Figure 1** [18].

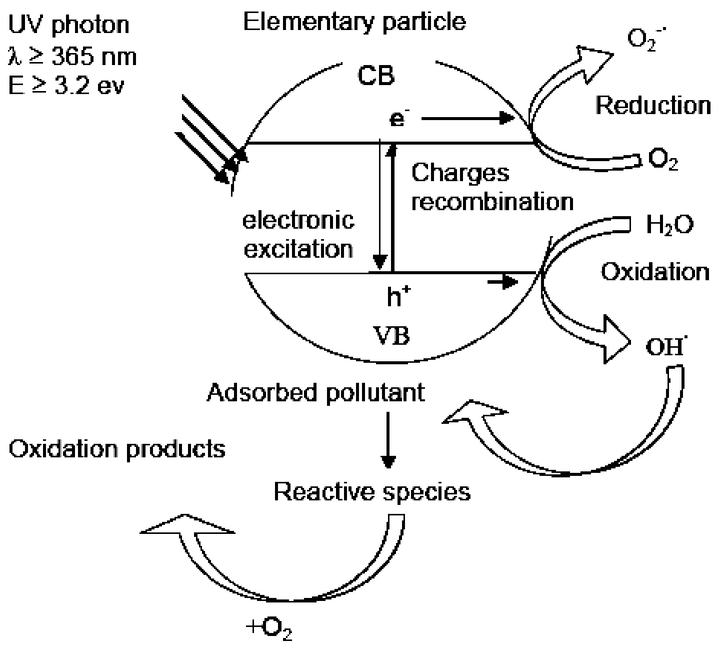


Fig. 1: Mechanism diagram of photocatalytic degradation.

Photodegradation of pollutant using TiO_2 with solar light is an economically process because the solar energy is an abundant natural energy source .This solar energy can be used instead of artificial light source. The artificial light sources need high electrical power which is costly and hazardous. Solar energy has been successfully used for photo catalytic degradation of pollutants [19-29].

In the present investigation we have under taken α-naphtholbenzein and examined the various parameters to find out the optimum conditions for removal of color and aromatic part of the dye.

Experimental

All experiments were carried out under similar conditions on sunny days of April-May between 11 Am and 2 Pm. 100ml three neck round bottom flask was used as reaction vessel which placed onto magnetic stirrer hotplate (obtained from GallenKamp) to reach the homogeneous mixing. The suspensions were magnetically stirred in the dark and light in the presence of dye only, dye-O_2 , dye-TiO_2 (supplied from Degaussa) and dye-TiO_2-O_2 . Fifty milliliters of dye solution with TiO_2 were continuously aerated by open part of the flask for complete mixing of reaction solution. At specific time intervals 3ml of the sample was withdrawn and centrifuged using centrifuge (supplied from 80-1 Table Top Low Speed Centrifuge Truip International Corp.120 cycle/min) .The electronic spectra and measurements(purchased from Shimadzu Uv-Vis. 1650 Spectrophotometer) of dye samples then determined .ethanol(supplied from Fluka) was used as a solvent of the dye. The concentration of α-naphtholbenzein used in all experiments was 40 ppm.

Results and Discussion

The preparation of calibration curve

The preparation of calibration curve solutions of α-naphtholbenzein — which have the structural formula as illustrated in **Figure 2** - at the range between (5-90) mg.L^{-1} were prepared using 96% ethanol as a solvent.

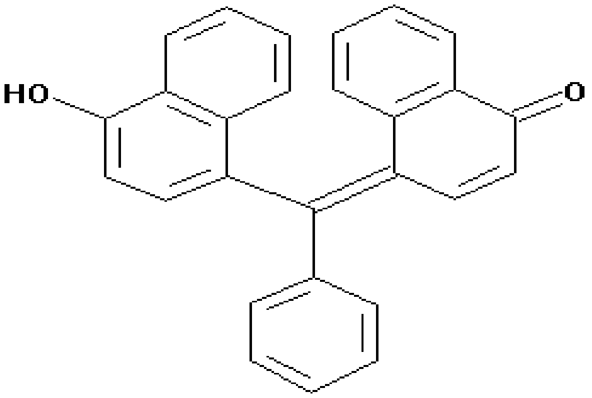


Fig. 2: The structural formula of α-naphtholbenzein.

The UV-Visible spectrum of the concentration 40 mg.L^{-1} was taken to identify the maximum wave length which was 463 nm (**Figure 3**) then the a absorbance at 463 nm was determined for each solution to represent the calibration curve by plot the values of a absorbance against the values of concentration which showed an straight line that obeyed the law of Lambert-Beer (**Figure 4**).

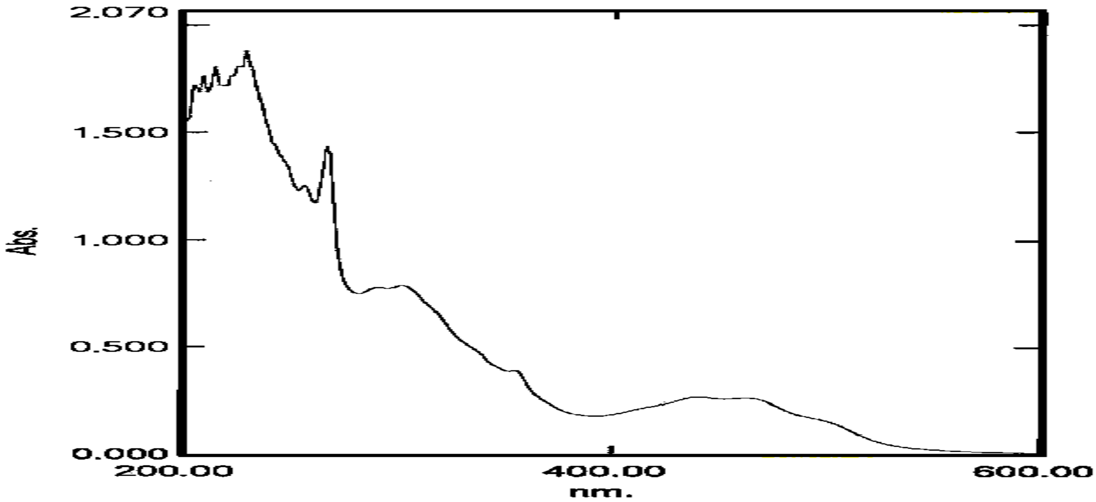


Fig. 3: The electronic spectrum of α-naphtholbenzein in 96 % ethanol.

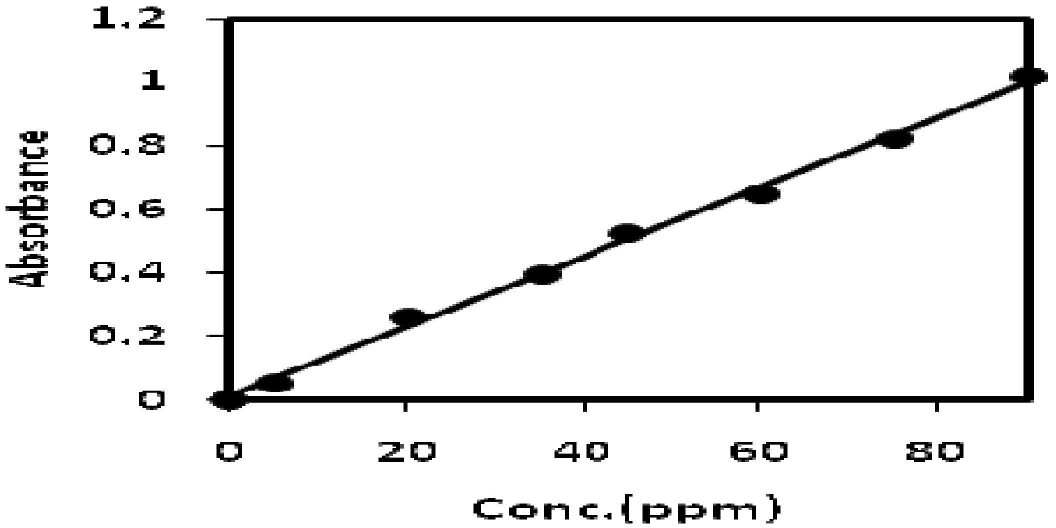


Fig. 4: Absorbance vs. concentration to prepare the calibration curve of α-naphtholbenzein at 463 nm.

The kinetics of photoreaction

The irradiation of the substance at different irradiation time in the presence of O_2 and catalyst at the range between (0.25–5.00) hr. was examined. The experiments showed that the percentage of conversion was increase with increasing the irradiation time (**Table 1** and **Figure 5**) and the optimum conversion % was at time 2.5 hr.

Table 1: The values of Co and C at different irradiation times of first order reaction of α-naphtholbenzein

Time (hr.) t	Initial conc.(ppm) Co	Residual conc.(ppm) C	Ln (Co/C)
0.5	40.00	38.79	0.03
1	40.00	37.28	0.07
1.5	40.00	36.00	0.11
2	40.00	35.13	0.13
2.5	40.00	34.00	0.16

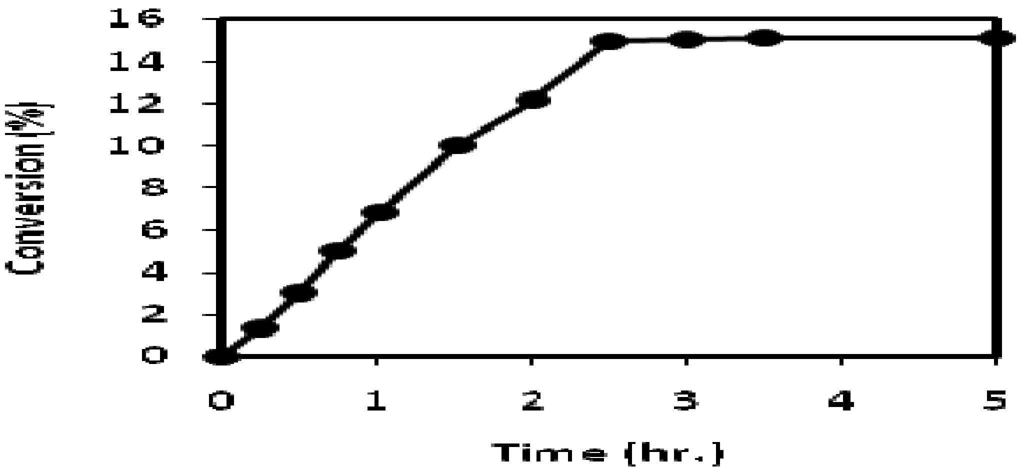


Fig. 5: Conversion % vs. irradiation time.

The reaction was from pseudo first order at range of time between (0.25–2.5) hr. because the plot of Ln (Co/C) against t (hr.) according to equation 4 –where Co is the initial concentration, (C) is the residual concentration and (t) is the time —yielded an straight line which represent the first order of reaction [30] and the rate constant (k) was determined by the slope (**Figure 6**).

Ln (Co/C) = kt......................... (4)

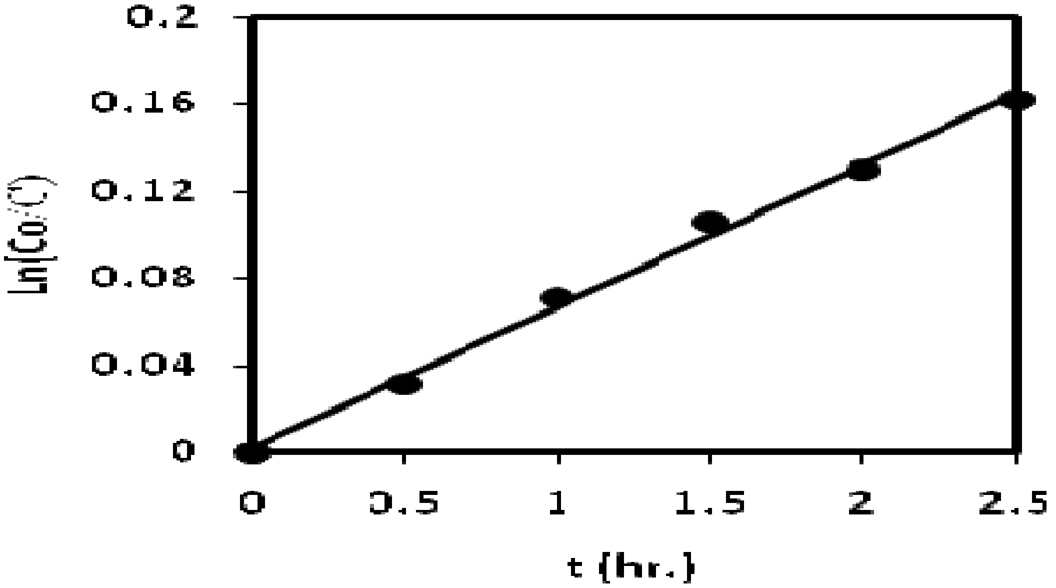


Fig. 6: Ln (Co/C) vs. irradiation time of first order reaction of photolysis process.

The effect of various conditions on the photolysis process

The reaction of α-naphtoholbenzien at different conditions in the presence of TiO_2, O2 and TiO_2-O_2 in the light and dark as illustrated by electronic spectra (**Figures 7** and **8**) was achieved.

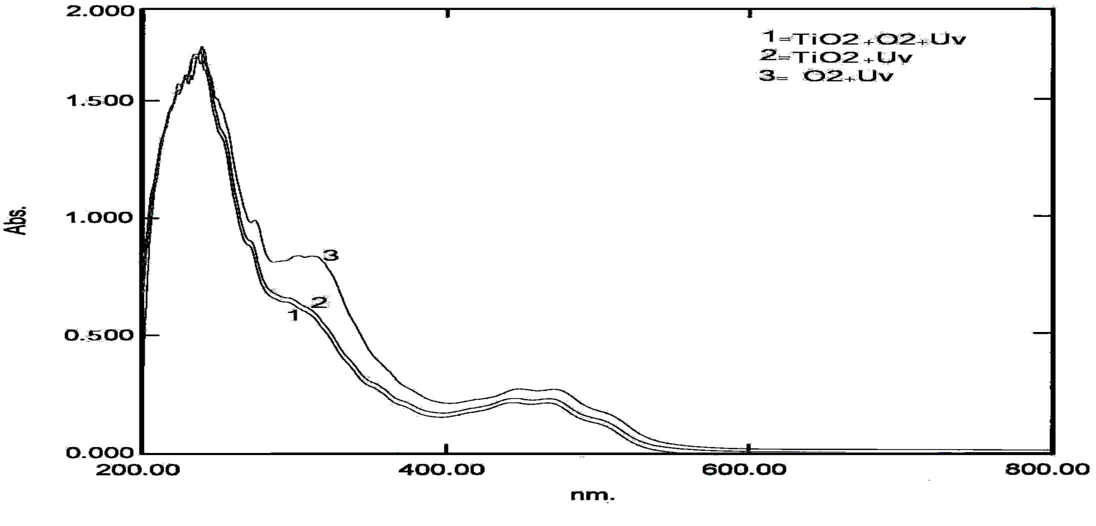
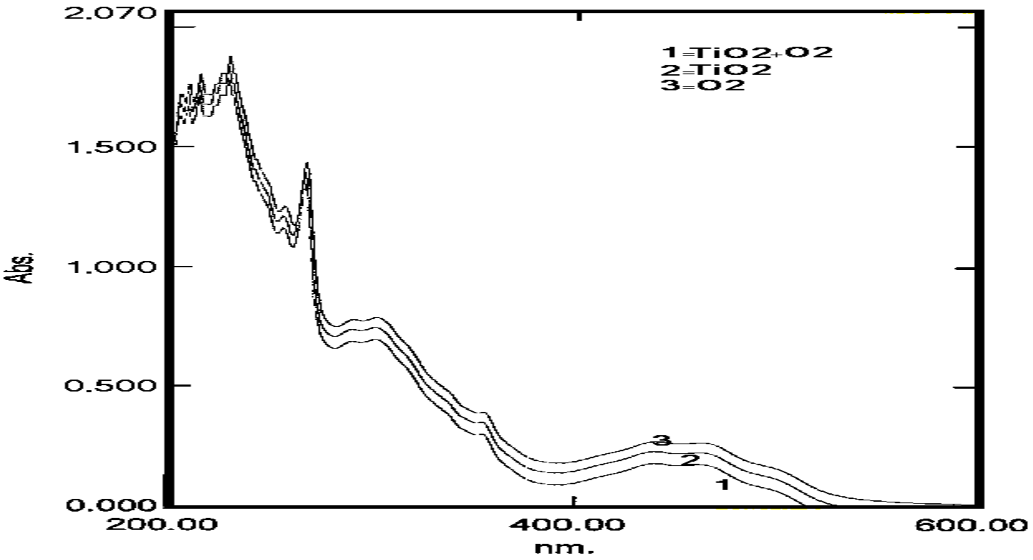


Fig.7: Electronic spectra of α-naphtholbenzein irradiated by Uv-Vis. light at different conditions. [α-naphtholbenzein] = 40 mg/L, [TiO_2] = 0.2 gm/ 50 mL, pH =6.4, solvent = 96 % ethanol.



ions.
[α-naphtholbenzein] = 40 mg/L, [TiO_2] = 0.2 gm/50 mL, pH =6.4, solvent = 96 % ethanol.

In the light reaction TiO_2 semiconductor particles illuminated yielded excited holes in valance band and excited electrons in conduction band. Both OH groups-founded at the surface of TiO_2-and molecular oxygen are induce the photolysis process [31, 32].

While in the dark reaction only adsorption process was formed at the surface of TiO_2 and molecular oxygen was unable to form the super oxidized oxygen ($\cdot{}^{-}O_2$). Thus, the percentage of conversion in the case of light was higher than that in the dark (**Figures 9** and **10**) and rate constant. Also the rate constant for light reaction was higher than in the dark reaction [33] (**Tables 2** and **3**).

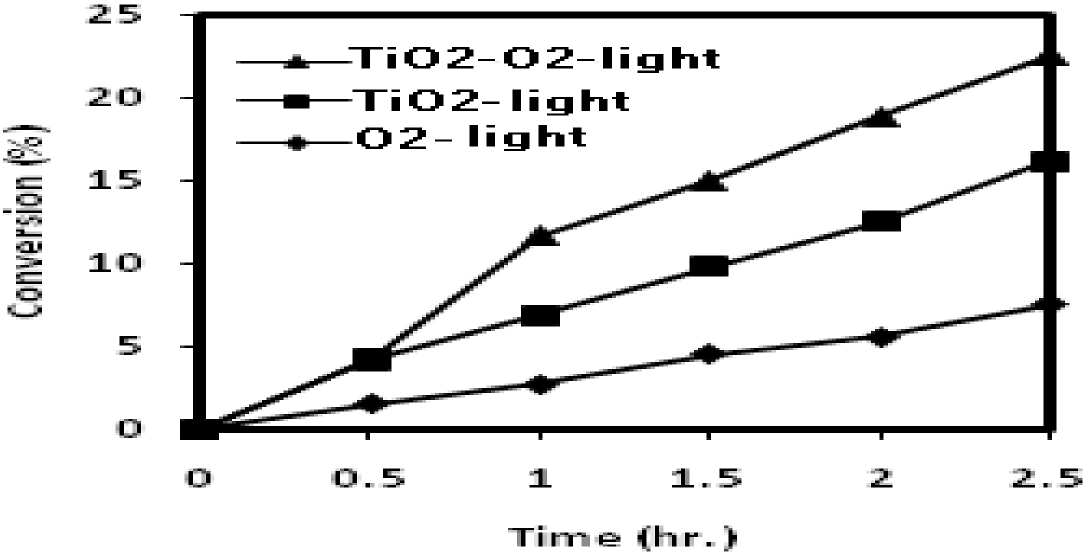


Fig.9: Conversion % vs. irradiation time of α-naphtholbenzein irradiated by Uv-Vis. light at different conditions. [α-naphtholbenzein]= 40 mg/L, [TiO_2] = 0.2 gm/ 50 mL, pH = natural, solvent = 96 % ethanol.

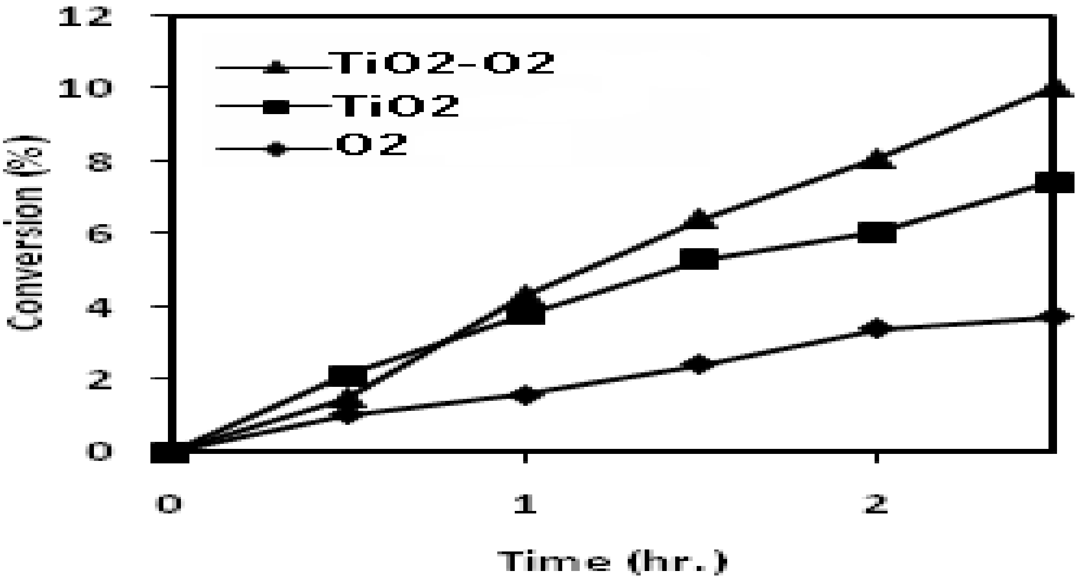


Fig. 10: Conversion % vs. irradiation time of α- naphtholbenzein in the absence of Uv-Vis. light at different conditions. [α-naphtholbenzein] = 40 mg/L, [TiO_2] =0.2gm/ 50 mL, pH = natural, solvent = 96 % ethanol.

Table 2: The values of rate constants of photolysis of α- naphtholbenzein in the presence of light at different conditions

Condition	**Rate constant(k)x10^{-3}**
O_2-light	31.1
TiO_2-light	65.7
TiO_2-O_2-light	102.2

Table 3: The values of rate constants of photolysis of α- naphtholbenzein in the absence of light at different conditions

Condition	**Rate constant(k)x10^{-3}**
O_2	14.7
TiO_2	27.2
TiO_2-O_2	44.4

The effect of TiO_2 loading

The amount of catalyst is one of the main parameters for the photolysis studies. In order to avoid the use of excess catalyst, it is important to find out the optimum loading for efficient removal of substance. Several authors have investigated the reaction rate as function of catalyst loading in the photolysis process [34-36]. The effect of catalyst weight of TiO_2 on the percentage of conversion of α-naphtholbenzein was investigated from 0.05 to 0.8 g as illustrated by electronic spectra (**Figure 11**).

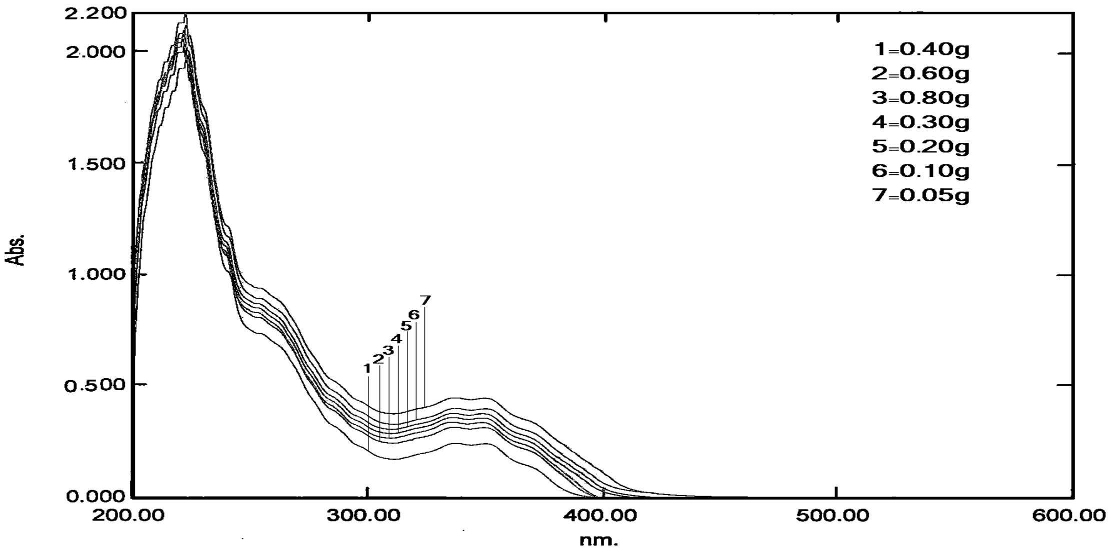


Fig. 11: Electronic spectra of α-naphtholbenzein irradiated by Uv-Vis. light at different TiO_2 loading. [α-naphtholbenzein] = 40 mg/L, pH=natural, solvent=96%ethanol

The results showed that the increase of catalyst weight from 0.05 to 0. 4 g Increases the photolysis rate due to (i) the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed (ii) the increase in the density of particles in the area of illumination. But at weights from 0.6 to 0.8 g the photolysis rates are almost constant [37] (**Figure 12** and **Table 4**).

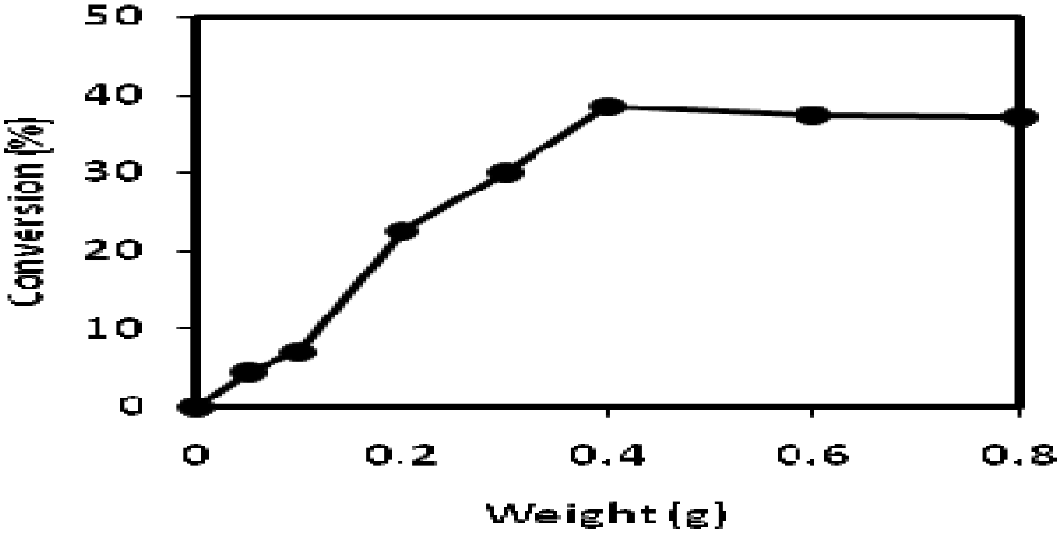


Fig. 12: Conversion % vs. weight of TiO_2 in the presence of Uv-Vis. light. [α- naphtholbenzein] = 40 mg/L, pH = natural, solvent = 96 % ethanol.

Table 4: The values of rate constants of photolysis of α-naphtholbenzein at different TiO_2 weights

Weight(g)	Rate constant (k)x10^{-2}
0.05	1.94
0.1	3.08
0.2	10.22
0.3	14.62
0.4	19.0
0.6	18.62
0.8	18.53

This may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration [36].

The effect of addition of H_2O_2

The effect of addition of H_2O_2 (2-16 mmol) on the photolysis process has been investigated as illustrated by electronic spectra (**Figure 13**).

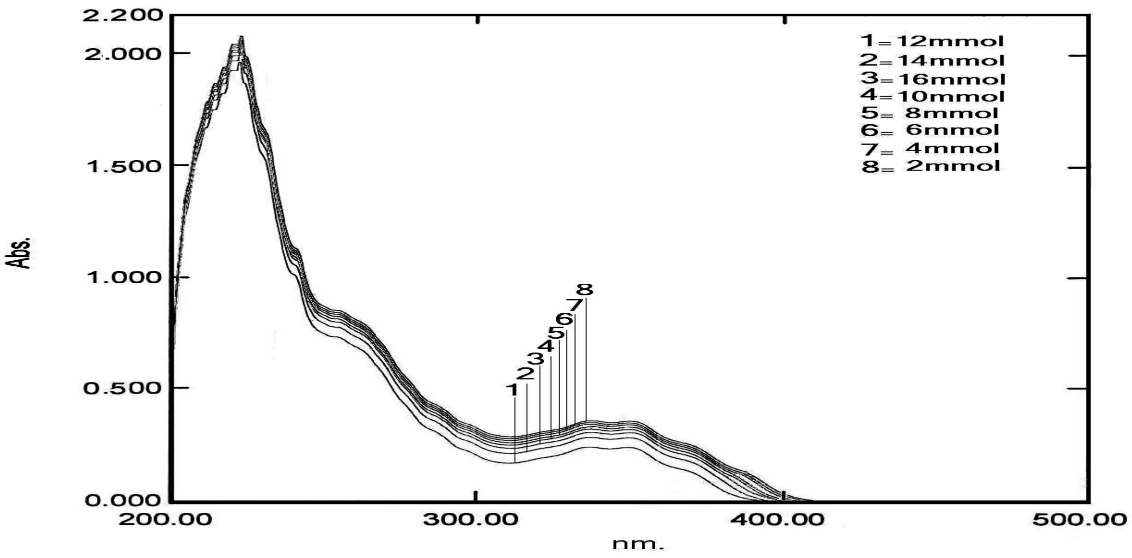


Fig.13: Electronic spectra of α-naphtholbenzein irradiated by Uv-Vis. light at different H_2O_2 concentrations, [α-naphtholbenzein] = 40mg/L,[TiO_2] = 0.4g/50mL, pH=natural, solvent = 96% ethanol.

The results are shown in **Figure 14** and **Table 5**. The addition of H_2O_2 (2-12 mmol) increases the photolysis rate, while further increase of H_2O_2 concentration from 12 to 16 mmol decreases the rate of photolysis process.

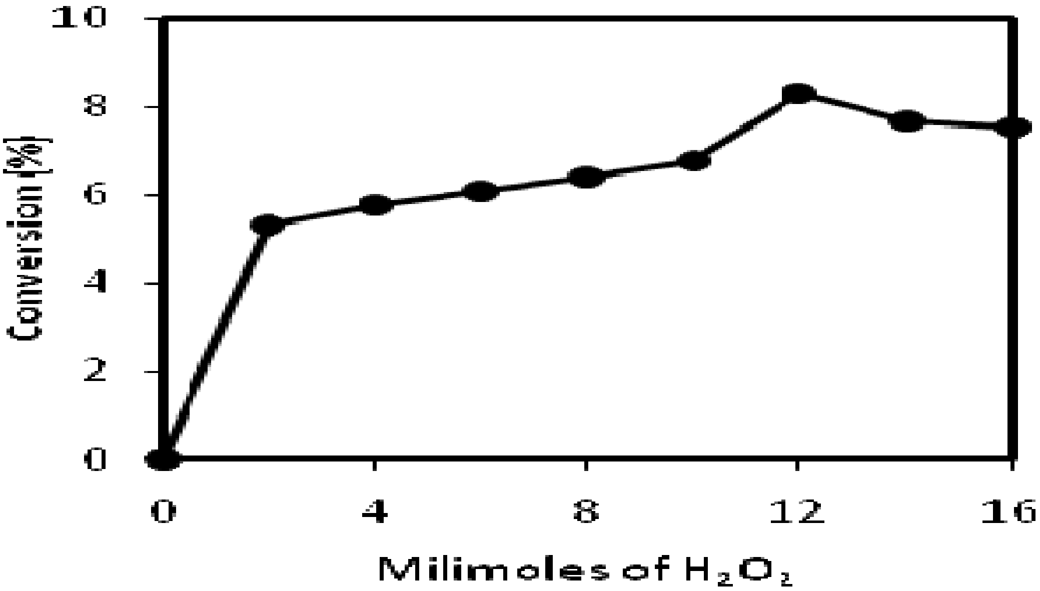


Fig.14: Conversion % vs. millimoles of H_2O_2 irradiated by Uv-Vis. light. [α- naphtholbenzein] = 40 mg/L, $[TiO_2]$ = 0.4 gm/ 50 mL, pH =natural, solvent = 96 % ethanol.

Table 5: The values of rate constants of photolysis of α-naphtholbenzein at different H_2O_2 concentrations

Milimoles	Rate constant (k)x10^{-2}
2	21.2
4	22.0
6	23.6
8	24.7
10	25.2
12	26.3
14	26.0
16	25.6

12 mmol of H_2O concentration appears to be optimal for the photolysis. The enhancement of photolysis by addition of H_2O_2 is due to increase in the hydroxyl radical concentration as in the following equations:

$H_2O_2 + e^- \rightarrow \cdot OH + {}^-OH$ .... (5)
H_2O_2 also reacts with superoxide anion to form ·OH radical:
$H_2O_2 + {}^-O_2 \rightarrow \cdot OH + {}^-OH + \cdot O_2$ ....(6)

While at high H_2O_2 dosage (12-16 mmol) the photolysis rate decreases due to its hydroxyl radical scavenging effect [38 and 39].

The effect of oxalate anion

Figure 15 illustrates the electronic spectra of α-naphtholbenzein at different oxalate concentrations.

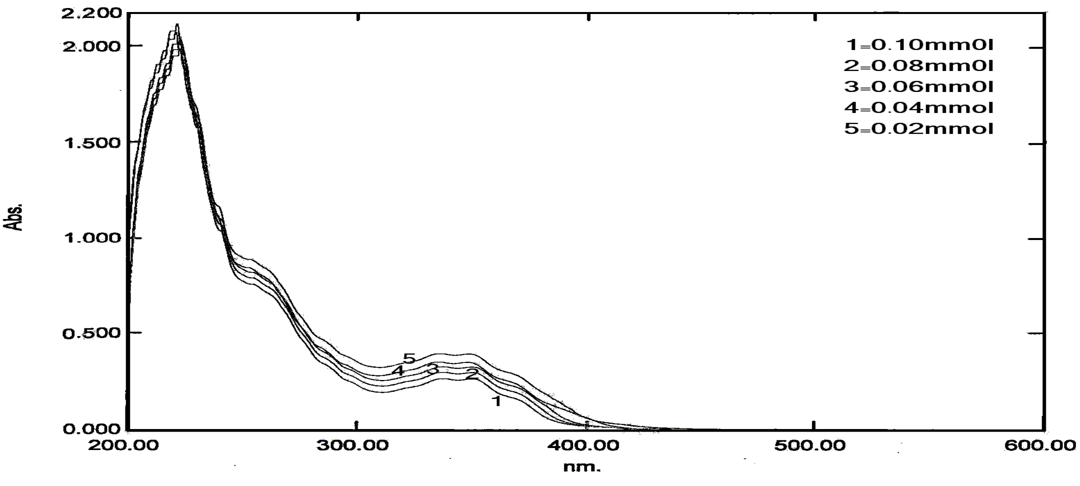


Fig.15: Electronic spectra of α-naphtholbenzein irradiated by Uv-Vis. light at different oxalate concentrations, [α-naphtholbenzein] = 40mg/L, [TiO_2] = 0.4g/50mL, pH=natural, solvent=96% ethanol.

It can be seen that increasing the oxalate concentration from 0.02 to 0.1 millimole increased α-naphtholbenzein removal efficiency (**Figure16** and **Table 6**) which is due to increasing the ·OH concentration [40].

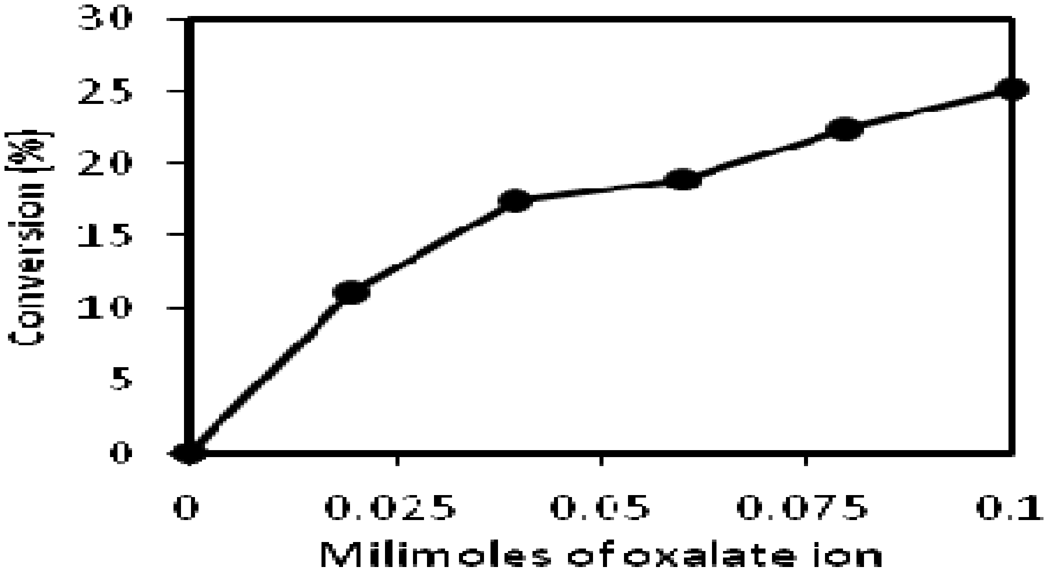


Fig. 16: Conversion % vs. millimoles of oxalate irradiated by Uv-Vis. light. [α-naphtholbenzein]= 40 mg/L, [TiO_2] = 0.4 gm/ 50 mL, [H_2O_2] = 12mmol, pH = natural, solvent=96 % ethanol.

Table 6: The values of rate constants of photolysis of α-naphtholbenzein at different oxalate concentrations

Milimoles	**Rate constant (k)x10^{-2}**
0.02	45.2
0.04	68..1
0.06	80.3
0.08	87.4
0.1	92.8

Conclusions

The optimum time of irradiation that gave a higher percentage of conversion of α-naphtholbenzein was at 2.5 hr. and the reaction was from pseudo first order at the range of time between (0.5-2.5 hr.).In the dark reaction the rate was approximately constant without any effect, while in the light the existence both Uv-vis. light and TiO_2 with molecular oxygen was the main role to increase the photolysis rate. The optimum weight of catalyst and H_2O_2 concentrations were 0.4 g and 12 mmole respectively. Also the experiments illustrated that the rate of photolysis increase with increasing oxalate anion concentration.

References

1) Adeyeye A and Osibanjo O. *Lewis Publishers.* **(1999),** 261.
2) Malato S. *Editorial CIEMAT*. Madrid, Spain. **(1999),** 22**.**
3) Blanco J and Malato S. *Natural Sciences. World Solar Programme*. (**2001**), 45.
4) Malato S, Blanco J, Vidal A, and Richter C. *J. Appl. Catal. B: Environ.* (**2002**), 37, 1.
5) Komann C, D.W. Bahnemann and Hoffmann M R. *J. Environ. Technol.* (**1991**), **25**, 494.
6) Hsiao C Y, Lee C L, and Ollis D F. *J. Catal.* (**1983**), 82, 418. Abstract.
7) Zahraa O, Chen H Y, and Bouchy M. *J. Adv. Oxid. Technol.* (**1999**), 4, 167.
8) Shifu C. *Environ. J. Sci.* (**1996**), 17, 33.
9) Chen L C and Chou T C. *J. Mol. Catal.* (**1993**), 85, 201.
10) Zheng S, Huang Q, Zhou J. and Wang B. J. *Photochem. Photobiol A: Chem.* (**1997),** 108, 235.
11) Poulios I and Aetopoulou I. *J.Environ. Technol.* (**1999**), **20**,479.
12) Epling G A and Lin C. *J. Chemosphere.* (**2002**), 46, 561.
13) Tang W Z and Ann H. *J. Chemosphere.* (**1995**), 31, 4171. Abstract.
14) Tang W Z, Zhang Z, Ann H, Quintana M O, and Torres D F. *J. Environ. Technol.* (**1997),** 18, 1.
15) Lakshmi S, Renganathan R, and Fujita S. *J. Photochem. Photobiol A: Chem.* (**1995),** 88,163.
16) Andreozzi R, Caprio V, Insola A, and Marotta R. *J.Catalysis Today.* (**1999), 53** 51.
17) Crittenden J C, Trussell R R, Hand D W, Howe K J, and G.Tchobanoglous."Water treatment: Principles and Design", 2nd edition, Wiley, New Jersey. (**2005**), 67.
18) Mills A and Le Hunte S. *J. Photochem. Photobiol.* (**1997),** 108, 1.
19) Wu H and Dong X. *J. Acta Energia Solaris Sinica*. (**1997),** 18, 380.
20) Wang Y and Fu Chin Y. *J. Biomed. Eng*. (**1998),** 17, 117.
21) Mathews L R. *J. Sol-Gel Sci. Tecnol.* (**1997),** 8,619.
22) Crittenden J C, Zhang Y, Hand D W, Perran D L, and Marchand E G. *J.Water Environ. Res*. (**1996),** 68, 270.
23) Waang Y. *J.Water Res.* (**2000),** 24, 990.
24) Minero C, Pelizzeti E, Malato S, and Blanco J. *J. Chemosphere*. (**1993),** 26, 2103. Abstract.
25) Herrmann J M, Disdier P J, Malato S, and Blanco J. *J. Appl. Catal. B. Environ.* (**1998),** 17, 15.
26) Neppolian B, Choi H C, Sakthivel S, Arabindoo B, and Murugesan V. *J. Chemosphere*. (**2002),** 46, 1173.
27) Sakthivel S, Neppolian B, Shankar M V, Arabindoo B, Palanichamy M, and Murugesan V. *J. Sol. Energy Mater. Sol. Cells*. (**2003),** 77, 65.
28) Kuo W S and Ho P H. *J. Chemosphere***.** (**2001),** 45, 77.
29) Minero C, Pelizzetti E, Malato S, and Blanco J. *J.Sol. Energy.* (**1996**), 56, 421.
30) Mirkhani V, Tangestaninejad S, Moghadam M, Habibi M H, and Rostami V A. *J. Iran. Chem. Soc***.** (**2009),** 6, 800.
31) Matthews R W. *J. Water Res*. (**1986),** 20, 569.

32) Kormann C, Bahnemann D W, and Hoffmann M R. ***J. Enviro.Sci. Tech.*** **(1991), 25**, 494.

33) Tanaka K and Reddy K. *J. Appl. Catal. B: Enviro.* **(2002),** 39, 305.

34) San N, Hatipoglu A, Kocturk G, and Cinar Z. *J. Photochem. Photobiol A: Chem.* **(2001),** 139,225.

35) Gouvea C A K, Wypych F, Moraes S G, Duran N, Nagata N, and Zamora P P. *J. Chemosphere*. **(2000),** 40, 96.

36) Saquip M and Munner M. *J. Dyes Pigments*. **(2002),** 53, 237.

37) Murugandham M and Swaminathan M. *J. Solar Energy and Solar Cells*. **(2004),** 81, 439.

38) Davis A P and Huang C P. *J.Water Sci. Technol.* **(1990),** 21,455.

39) Malato S, Blanco J, Richter C, Braun B, and Maldonado M I. *J.Appl. Catal. B: Environ.* **(1998),** 17, 455.

40) Safarzadeh A A , Bolton J R, and Cater S R. *J. Water. Res.* **(1997),** 31, 787.

Acylation of Synthesized Schiff Bases Derived From-2-Amino-1, 3, 4-Thiadiaizol

Asrra Mohammed Jawad
Department of Pharmaceutical Chemistry-College of Pharmacy-University of Kufa

الخلاصة

إن اسيلة بعض أنواع قواعد شيف تم بنقاوة وانتاج عاليين ،حيث تم في المرحلة الاولى مفاعلة ٢-امينو-٤,٣,١-ثايادايازول مع بعض الأنواع من الالديهدات جميعها اروماتيه لتحضير قواعد شيف كمشتقات للثايادايازول، اما في المرحلة الثانية فقد تم اسيلة هده المشتقات باستخدام انهدريد الخليك، تم تشخيص كل المشتقات المحضرة بواسطة مطيافية الأشعة تحت الحمراء IR، وجهاز التحليل الدقيق للعناصر(C.H.N.S).

Abstract

Acylation some types of Schiff bases were achieved with a high yield and purity, the first step was performance by treated 2-Amino-1, 3, 4,-thiadiazole with an aromatic aldehydes to obtain a Schiff bases as thiadiazole derivatives, the second step included reaction of synthesized Schiff bases with an acetic anhydride to produce the acylation of Schiff bases. The identification of synthesized derivatives, were established through IR spectroscopy and micro elemental analysis (C.H.N.S) data.

Key words: *2-Amino-1, 3, 4,-thiadiazole, Schiff bases, Acylation.*

Introduction

Schiff bases is nitrogen analog of an aldehyde or ketone which the C= O group is replaced by C= N group [1] the formation of a Schiff bases from an aldehyde or ketone is a reversible reaction and generally take place under acid or base catalysis or upon heating [2], The mechanism of Schiff bases formation depend up on neuclophilic addition to the carbonyl group in this case the nucleophile is amine [3].

Acylation of Schiff bases have a large number of synthetic uses in organic chemistry, reaction of acylation products with primary amines results in adducts which tend to decompose to anew imines and primary amine [4,5] , the addition of hydrogen cyanide to acylation products occurs readily and provides for the synthesis of amino acid (Strecker synthesis) [6], the acylation products have reported in the literature posseting , antibacterial, antifungal , antimicrobial , anti-inflammatory and antitumor activities [7].

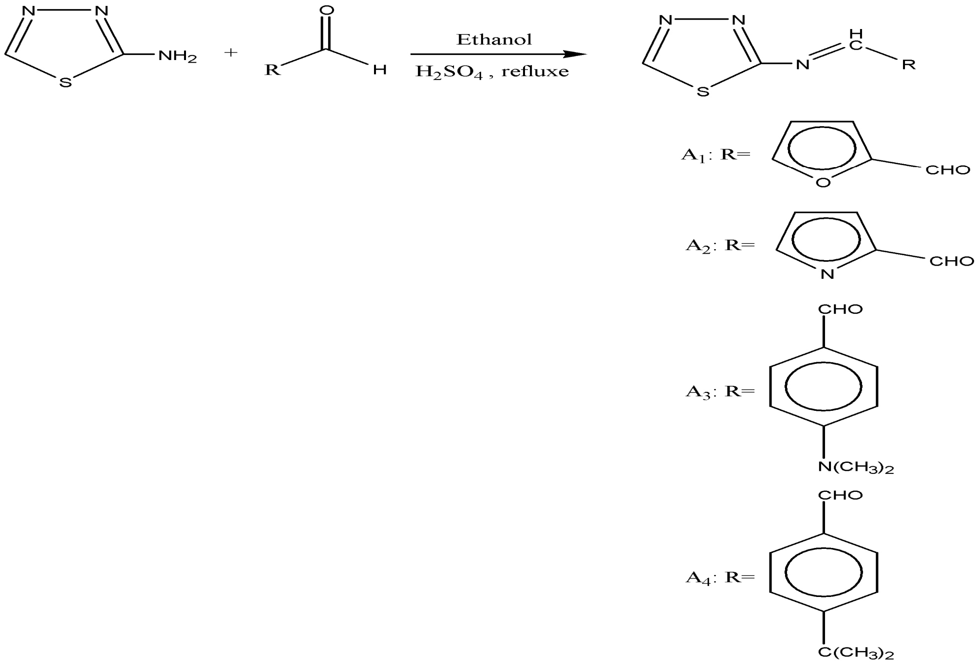
The certain polymeric acylation derivatives have also been found to possess antitumor activity , they have the highest degree of hydrolysis at pH 5 and the solubility in water it also increase at this pH, the anti-tumor activity of acylation products towards anti-tumor increase considerably with the slight increase in water solubility [8]. They also appear to be important intermediates in a number of enzymatic reaction for example transamination reaction, transamination reactions are catalyzed by class of enzymes called transaminase are found in mitochondria and cytosol of e-eukaryotic cells [9]. Bio synthesizes of prophyrin for which the glycine is precursor is another important path way which involves the intermediates formation of acylation products [10].

An aim of the search is synthesis a stable acylation derivatives of Schiff bases, with a high yield and purity in a mild conditions.

Experimental

Procedure for preparation Schiff bases

To stirred solution 0.01 mole in 30 ml ethanol of -2-Amino 1,3,4-thiadiazol, were add 0.01 mole in 30 ml ethanol of appropriate aldehydes, and 2-3 drops of concentrated sulfuric acid (**Scheme 2**) the resultant mixture in each case was then heated under reflux for 3 hours .



Scheme 2: The Synthesized Schiff Bases

The reaction mixture in each case was reduced to 10- 15ml and kept at room temperature for1/2 an hour , the solid thus formed in each case was collected by section filtration and recrystallization from aqueous ethanol. The physical data of synthesized compounds are given in **Table 1.**

Table 1: The physical and elemental analysis (C.H.N.S) data

Comp.	Molecular formula	M.W	Rf	M.P (C^0)	Color	% C		%H		%N		%S	
						Calc	**Found**	**calc**	**found**	**Calc**	**Found**	**Calc**	**found**
A1	$C_7H_8N_3SO$	181	٠.٧٦	184	Yellow	46.4	46.1	3.8	3.5	23.2	23.45	17.6	17.8
A2	$C_7H_8N_4S$	180	٠.٨٥	178	Yellow	46.66	46.8	3.88	3.45	31.11	31.38	17.7	17.95
A3	$C_{11}H_{13}N_4S$	233	٠.٨	98	yellow	56.65	56.9	5.57	5.34	24.03	24.25	13.7	13.79
A4	$C_{12}H_{14}N_3S$	232	٠.٧٥	122	Green	62.06	62.4	6.03	6.01	18.1	18.33	13.7	13.45
B1	$C_{10}H_9N_3O_4S$	266	٠.٦٦	٢٤٣	Orang	44.9	45.3	3.3	2.8	15.7	16.2	11.9	12.2
B2	$C_{10}H_{10}N_4O_3S$	267	٠.٧٢	١٦٦	yellow	45.1	44.8	3.75	3.4	21.1	21.6	11.8	11.3
B3	$C_{14}H_{16}N_4O_2S$	303	٠.٨٧	٢٥٦	Brown	61.1	61.5	5.26	4.9	18.8	19.3	10.4	10.7
B4	$C_{15}H_{17}N_3O_2S$	304	٠.٨٤	٢٨٩	Brown	59.4	58.8	5.6	4.7	13. 6	14.2	10.5	10.1

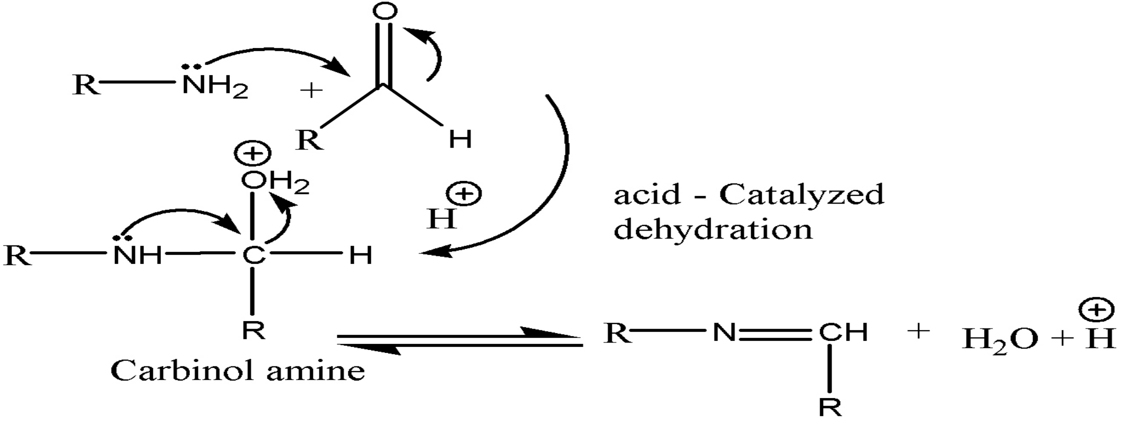
M.W: molecular weight, Rf: rate of flow, M.P: melting point, Calc: calculation

Procedure for Schiff base derivatives acylation

The mixture of Schiff base derivatives (0.01 mole) and 10 ml acetic anhydride was dissolved in 25 ml ethanol with few drops of conc. H_2SO_4 (**Scheme 3**) the reaction mixture was refluxed for four hours at 100°C. The reaction mixture was then concentrated, allowed to cool, the solid product obtained was filtered, washed with water and recrystallized using methanol. The physical data of synthesized compounds are given in **Table 1.**

Results and Discussion

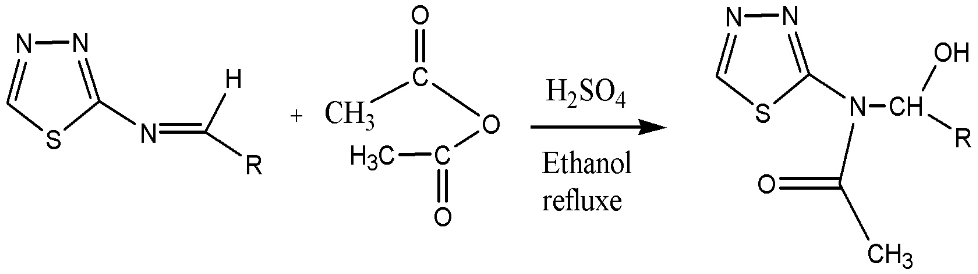
The schiff bases A_1-A_4 were prepared by refluxing equimoler (0.01mol) quantities of-2-Amino-1,3,4-thiadizaole, and the respective aldehydes (**Scheme 2**), the mechanism of neuclophilic addition(in this case, aromatic amine) involve formation unstable intermediate called carbinolamine which loss water by acid catalyzed pathways, addition of conc. H2SO4 must be not more than few drops because if the amine is protonated well be becomes non neuclophilic and the equilibrium is pulled to the left, so intermediate formation cannot occur [11] (**Scheme 1**).



Scheme 1: The steps formation of carbinol amine.

The Schiff bases acylation derivatives (B1-B4) were a chivied by reflux equimolar quantities of acetic anhydride and Schiff bases (A1-A4). It has long been known that Schiff bases of aromatic amines could be readily acrylate with acetic anhydride.

The reaction involves an addition across the HC=N bond to form a stable compound, this reaction is unique in that the acetic anhydride itself capable of acylation and reducing the Schiff base in a single reaction [12, 13] (**Scheme 3**).



Scheme 3: The Schiff bases acylation derivatives

The identification and purity of the synthesized derivatives was confirmed by T.L.C values.(benzene,chloroform 9:1)they appear distinguishable differences between the Rf of Schiff bases and Rf of acylation derivatives values (rate of flow **Table 1**),yet structures and functional groups were identify by FT-IR spectroscopy and C.H.N.S data (**Table 1**).

IR Spectra of Schiff bases derivatives

The IR Spectra for the derivatives A_1-A_2 showed band resulting from HC=N stretching at1630 cm^{-1}[14], and thiadizol stretching (C=N)at 1620cm^{-1}[14], in addition to these bands the spectrum of A_2 showed strong band at 3225cm^{-1} resulting from the NH stretching of pyrrol, in case of Schiff bases $A_3$and A_4 in addition to the azomethine stretching (HC=N) at

1635cm^{-1} and thiadizol stretching at1605cm^{-1}, C=C aromatic stretching at 1590 cm^{-1},C-H aromatic stretching at 3030cm^{-1},C-H stretching of alkyl group at 2885 and 2780 cm^{-1} and C-N stretching at 1375cm^{-1}.

IR Spectra of Schiff bases acylation derivatives

The IR Spectra for the derivativesB_1-B_2 showed band resulting from C=O stretching at1670 cm^{-1} ,and OH stretching at 30190cm^{-1}, in addition to these bands the spectrum of B_2 showed a strong band at 3230cm^{-1} resulting from the NH stretching of pyrrol, in case of compounds B_3-B_4 in addition to the C=O stretching at 1685cm^{-1} and thiadizol stretching at1615cm^{-1} ,showed OH stretching at 3000 cm^{-1},C-H aromatic stretching at 3030cm^{-1},C-H stretching of alkyl group at 2885 and 2780 cm^{-1} and C-N stretching in 1375cm^{-1}.

References

1) Campbell K N, Somers H, and Commpbell B K. *J. Am. Chem. Soc.* **(1944),** 66 , 82
2) Hine J and Yeh CY. *J. Am. Chem. Soc.* **(1967),** 89, 2669.
3) Savich I A, P kaev A K, and Hnaive S N. *Vestnik Moskor Univ.* **(1956),** H, 225 .
4) Tazoki H and Miyano K. *J. Am. Chem. Soc.* **(1999),** 85, 9769.
5) Layer R W. *J. Chem. Rev.* **(2003),** 63, 989.
6) Harada K. The Chemistry of the Carbon –Nitrogen Double Bond. 3rd Edition, Spatial, Interscince, New York. **(1970),** p255.
7) Sha Y W and Wanig Y. *E.SO. Chim. J. Org. Chem.* **(2001),** 21, 102.
8) Ittle D and Johanson L K. *J. Chim. Rev.* **(2000),** 100, 1164.
9) Karia F D and Parsania P L. *Asian J. Chem.* **(1999),** 11, 991.
10) Sari N, Arsalan S, Logo E, and Sakiyar I. *Journal of science.* **(2003),** 283.
11) Ghwan W H, Lrwaro F, and Josief B A. *J. Org. Chem.* **(1973),** 12, 1344.
12) Bleman J H and Macdewall J W. *J. Org. Chem.* **(1994),** 26, 1437.
13) Brockmann H and Franco B. *J. Bio.Org. Molecule.* **(2005),** 37, 455.
14) Whily J. The Systematic Identification of Organic Compounds. 2nd Edition. The life science, New York, **(2008).**

Synthesis, Identification and Study of the Biological Activity of Some New Aminoacetylenic Isoindoline-1, 3-Dione Derivatives

Asaad Hashim Aneed* **Naji Musa Ali****
*Department of Chemistry-College of Science-University of Kufa. **Department of Pharmaceutical Chemistry- College of Pharmacy-University of Kufa
E-mail: asaadha@sci.kuiraq.com

الخلاصة

حضرت مشتقات امينو استيلينية جديدة للفثاليمايد ، من خلال تحويل الفثاليمايد الى ملح البوتاسيوم المقابل بتفاعله مع هيدروكسيد البوتاسيوم ثم الكلة ملح الامايد باستخدام البروبارجيل برومايد للحصول على بروبارجيل فثاليمايد المطلوب (A_1). وللحصول على المشتقات الامينو استيلينية الجديدة للفثاليمايد(A_6-A_2) اجري تفاعل مانخ الذي تضمن تكاثف كل من المركب (A_1) مع بعض الديهايدات ، بوجود امينات حلقية ثانوية مثل المورفولين والبايبريدين.شخصت المركبات المحضرة باستخدام FT-IR و ^{1}HNMR وتحليل العناصر ، وقد تمت دراسة الفعالية البايولوجية لهذه المركبات باستخدام احد انواع البكتريا بروتس فلكاريس.

Abstract

A number of aminoacetylenic isoindoline-1,3-dione (phthalimide) were prepared through the reaction of phthalimide with potassium hydroxide then alkylation process were carried out for this salt in order to afford N-propargylphthalimide(A_1) .The Mannich reaction (three component one pot reaction) was carried out by using the N-propynylphthalimide (A_1), with different aldehydes in presence of morpholine or piperidine, as a secondary amines, to yield the desired compounds(A_2-A_6).The FT-IR, ^{1}HNMR and elemental analysis were consistent with the assigned structures, these compounds also have been tested biologically against bacteria *Proteus vulgaris*.

Key words: *phthalimide, Mannich reaction, piperidine, morpholine.*

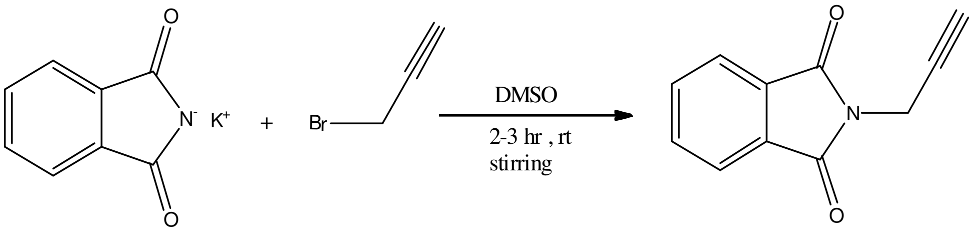
Introduction

Nitrogen heterocyclic compounds are important part of the chemical structures of many natural and synthetic products with a large number and variety of applications and a wide range of properties, from medical to toxic effects. Among the bicyclic aromatic nitrogen heterocycles phthalimides, this is an interesting class of compounds with a large range of applications [1]. Phthalimide and its derivatives are very important compounds. They are used in the synthesis of anti-inflammatory [2] antipsychotic[3] antimicrobial [4] antiandrogen [5] exhibitcytostatic[6] and other agents for treating tumor necrosis factor [7] on the other hand certain phthalimide derivatives are used as herbicides and for reducing bacterial contamination. In industry field derivatives containing phthalimide served as antioxidant [7], anion exchanger resins [5], and heat resistant polymers [8].

Experimental

Synthesis of 2-(prop-2-ynyl) isoindoline-1, 3-dione (A_1)

In order to synthesis 2-(prop-2-ynyl) isoindoline-1, 3-dione 1 g (5 mmol) of potassium phthalimide was reacted with 0.70 ml (6 mmol) of propargyl bromide. The reaction mixture was stirred at room temperature and monitored using thin layer chromatography (**TLC**), after 2-3 h, it was poured into 50 ml of cold water and stirred for 15 min. The resulting crude product was filtered, dried and crystallized from appropriate solvent to give (A1) as colorless needle-like crystals. M.p. 150-152°C (65%) [9].



A_1

Scheme1: Synthesis of N-propynylphthalimide (A_1)

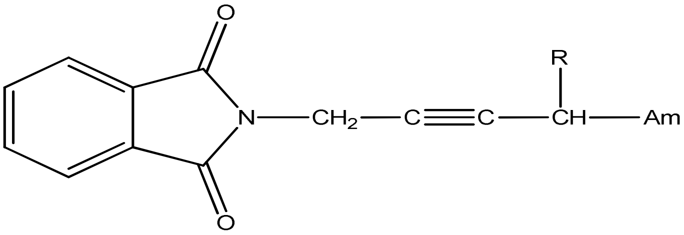
Table 1: Physical properties of (A_1)

Comp. No.	Chemical Formula	M.P. °C	Yield %	Color
A_1	$C_{11}H_7NO_2$	150-152	65	Colorless needle-like crystals

The compound (**A_1**) mentioned above indeed is the starting point for this study , that is the terminal alkyne possessing an acidic hydrogen and can take part in a very important class of reactions in organic chemistry which known as *Mannich reaction.*

Synthesis of Aminoacetylenic isoindoline-1, 3-dione (A_2-A_6)

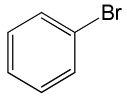
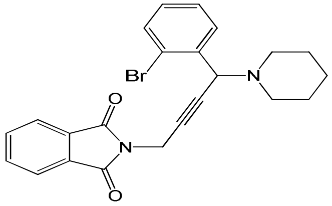
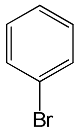
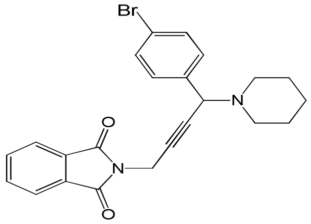
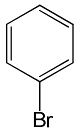
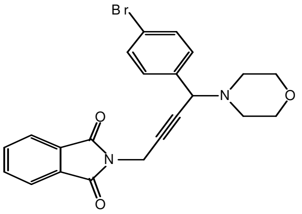
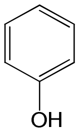
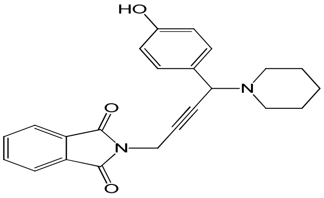
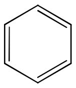
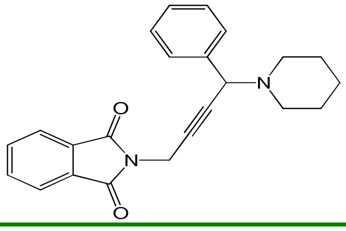
General Procedure: A mixture of 2-(prop-2-yn-1-yl) isoindoline-1, 3-dione (**A_1**) (0.005mole), an aldehyde (0.005 mole), secondary amine (0.005 mole) and cuprous chloride catalytic amount in peroxide-free dioxin (20) ml was refluxed for 1h. After cooling, (100) ml of water was added and the crude product was recrystallized from appropriate solvent to afford the desired compounds.



Scheme2: N-(4-(t- amino-l-yl) but-2-yn-1-yl) isoindoline-1, 3-dione

The general structure that demonstrates in **Scheme 2** represented to the synthesized aminoacetylenic isoindoline-1, 3-dione compounds. **Table 2** shows the derivatives which were synthesized.

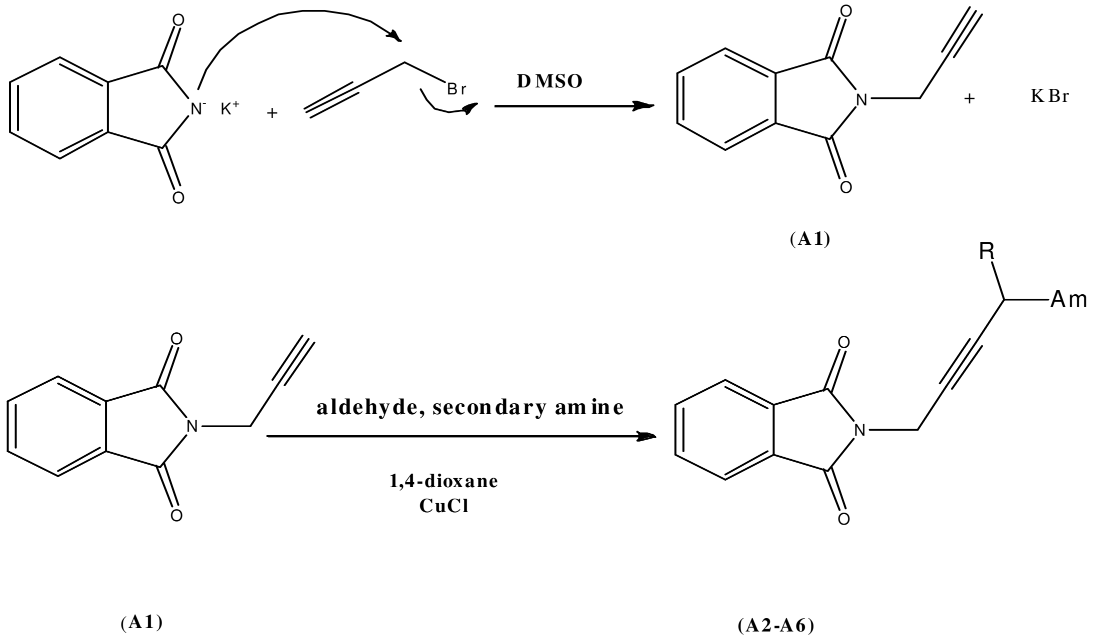
Table 2: Aminoacetylenic Isoindoline-1, 3-Dione Derivatives

Comp.	R	Am	Structure
A_2	 *Ortho*-bromophenyl	Piperidine	
A_3	 *Para*- bromophenyl	Piperidine	
A_4	 *Para*- bromophenyl	Morpholine	
A_5	 *Para*-ydroxyphenyl	Piperidine	
A_6	 Phenyl	Piperidine	

Results and Discussion

Isoindoline-1, 3-dione (phthalimide) is acidic *($pk_a=8.3$)*. It forms salts with various metals such as potassium and sodium due to its high acidity caused by the electrophilic carbonyl groups attached to the nitrogen atom that allowed reacting phthalimide with potassium hydroxide (acid base reaction) to give phthalimide potassium salt in order to activate the nucleophilicity of nitrogen atom. We are using phthalimide as starting material to synthesis a numder of novel aminoacetylenic compounds.

Phthalimide served as starting material and was converted to the corresponding potassium salt through reaction with potassium hydroxide. Alkylation of the imide salt with propargyl bromide afforded the desired N-propynyl phthalimide. The Mannich reaction of N-propynyl phthalimide, formaldehyde and other benzaldehyde derivatives, with morpholine or piperidine, as a secondary amines, in peroxide-free dioxin in the presence of catalytic amount of cuprous chloride under various basic, acidic, solvent and temperature conditions, resulted in a novel aminoacetylenic Isoindoline-1, 3-dione derivatives. The following **Scheme 3** illustrates the synthetic strategy.



where R= phenyl or substituted phenyl
Am= secondary amine

Scheme 3: Synthetic strategy.

Table 3: Physical properties of prepared compounds

Comp. No.	Molecular Formula	M.P.	Yield%	Color
A_2	$C_{23}H_{21}BrN_2O_2$	84-86	76	Brown
A_3	$C_{23}H_{21}BrN_2O_2$	135-137	75	White
A_4	$C_{22}H_{19}BrN_2O_3$	145-147	70	Light yellow
A_5	$C_{23}H_{22}N_2O_3$		55	Reddish brown
A_6	$C_{23}H_{22}N_2O_2$	96-98	63	Light yellow

Table 4: IR, NMR data and CHN analysis of prepared compounds

Product	IR(KBr)cm^{-1}	^{1}H-NMR (DMSO) (PPM)	CHN analysis	
			Calc.	Found
A_1	νCH 3294 ν C≡C 2245 νC=O 1720, 1770 ν C=C 1612, 1553, 1396			
A_2	ν C≡C 2252 ν ArH 3061 ν AliH 2931,2852, 2806 ν C=O 1768,1720 ν C=C 1610,1421, 1392	δ 1.9 (s,1H) methine δ 2.3 (s,2H) methylene δ 3.3(s,10H)piperidine δ 6.9 (s,4H) phenyl attached to methine δ 7.3 (s,4H) benzene ring of phthalimide	C= 63.17 H= 4.84 N= 6.41	C= 64.09 H= 4.78 N= 6.08
A_3	ν ArH 3067 ν AliH 2933,2852, 2812 ν C=O 1770,1720 ν C=C 1612,1485	δ 1.9 (s,1H) methine δ 2.2 (s,2H) methylene δ 3.5(s,10H)piperidine δ 6.9-7.3(m,4H) phenyl substituted at para position δ 7.0 (s,4H) benzene ring of phthalimide	C= 63.17 H= 4.84 N= 6.41	C= 63.48 H= 5.49 N= 7.15
	ν ArH 3061 ν AliH 2956,2827 ν C=O 1772,1722	δ 1.9 (s,1H) methine δ 2.3 (s,2H) methylene δ 3.4-3.7	C=60.15 H= 4.36 N= 6.38	C= 60.16 H= 4.56 N= 5.65

A_4	ν C=C 1615,1420, 1394	(m,8H)morpholine ring δ 7.0-7.6(m,4H) phenyl substituted at para position δ 7.3 (s,4H) benzene ring of phthalimide
A_5	ν C≡C 2260 weak ν ArH 3097 ν AliH 2937,2821 ν C=O 1770,1720 ν C=C 1612, 1467	δ 1.7 (s,1H) methine δ 2.1 (s,2H) methylene δ 3.5(s,10H)piperidine δ 7.0-7.2 (m,8H) two aromatic rings δ 11.8 (s,1H) phenolic proton
A_6	ν C≡C 2260 weak ν ArH 3061 ν AliH 2931, 2852 ν C=O 1770 ,1720 ν C=C 1612, 1465, 1396	δ 1.9 (s,1H) methine δ 2.3 (s,2H) methylene δ 3.3(s,10H)piperidine δ 6.9(s,4H) phenyl attached to methane δ 7.3 (s,4H) benzene ring of phthalimide

The biological activity of the effect of some prepared compounds in this research (**A_2**,**A_3** and **A_4**) on growth of one type of bacteria *Proteus vulgaris* were studied and the results are shown on **Table 5**. Meantime, the observable inhibition zone was determined during prepare concentration by dilution with **DMSO** (10, 20, 30 and 40) mg/ml of each compound.

Table 5: Inhibition zone of some compounds using Tode's method

Conc. Comp. No.	10 mg/ml	20 mg/ml	30 mg/ml	40 mg/ml	Control DMSO
A_2	R	R	R	R	R
A_3	R	R	R	R	R
A_4	R	R	R	R	R

All tested compounds were inactive against the studied bacteria *Proteus vulgaris* as the **Table 5** exhibit.

References

1) Ribeiro Silva M A V, Claudia Santos P F, Monte M J S, and Sousa C A. *Journal of Thermal Analysis and Calorimetry*. (**2006**), 83, 533-539.

2) Emerson, Falcao S, Sebastiao, Mole J, Rajendra, and Srivastava M. *Journal of Medical Chemistry*. (**2006**), 41, 276-282.

3) Imanzadeh G H, Khalafi-Nezhad A, Zare A, and Hasaaninejad A. *Journal of the Iranian Chemical Society*. (**2007**), 4, 229-237.

4) Suaad, Al-Majidi M H Z, and Al-Messri A K. *Journal of Al-Nahrain Chemistry*. (**2007**), 10, 30-37.

5) Krishnakumar V, Balach andran V, and chithambarathanu T. *Spectochimica Acta part A*. (**2005**), 62, 918-925.

6) Anna W and Krzysztof W. *Carbohydrate research*. (**2008**), 343, 2680-2686.

7) Marco L, Fiammetta F, and Gian F. *Tetrahedron Letters*. (**2007**), 48; 5331-5334.

8) Hansong C, Zhengming Li, and Yafeng H. *Journal of agriculture food chemistry*. (**2000**), 48, 5312-5315.

9) Lucky O, Okunrobo, Usifoh C O, and Gerhard K E. Polish Pharmaceutical Society. (**2006**), 63, 25-31.

Quantum Mechanical Calculations of Electronic Structure for Some Azo Imidazole Compounds

Khidhir Abd Al Hussein Khidhir* Heider Abdul Razzaq Abdul Hussein, and Hamieda Edan Salman***
*Dept. of Chemistry, College of Education for pure science, University of Kerbala
**Bio–Chemical Laboratory, University of Kufa
E-mail: *hei_chem@yahoo.com*

الخلاصة

أجريت حسابات ميكانيك الكم باستخدام إحدى الطرق شبه التجريبية وهي نموذج (PM3) المتضمنة الحصول على الشكل الهندسي ذي الطاقة الأقل لسبعة من مركبات الآزو والمسماة اختصاراً (A, B, C, D, E, F, G). وقد تم حساب الأبعاد الهندسية (قيم أطوال وزوايا التآصر) وحرارة التكوين وعزم ثنائي القطب وطاقة أعلى مدار جزيئي مشغول (E_{HOMO}) وطاقة أوطئ مدار جزيئي فارغ (E_{LUMO}) وطاقات التأين والشحنات والكثافات الالكترونية كما تم دراسة تأثير المجموعة المعوضة على الاستقرارية بالاعتماد على Isodesmic reactions (مقياس الاستقرارية ، Δ). وقد تبين من خلال النتائج إن طول الآصرة (C-X) حيث ($X = CH_3, NO_2$)، تكون اكبر من (C-H)، وان طول الآصرة ($C-NO_2$)يكون اكبر من ($C-CH_3$)، كما إن طول الآصرة ($N_7=N_8$) يمتلك أعلى قيمة عند الموقع ميتا، واقل قيمة عند الموقع اورثو وبارا في حالة كون المجموعة المعوضة (CH_3) و (NO_2) على التوالي. كما أشارت النتائج إلى إن المركبين (D، F) يمتلكان اقل حرارة تكوين، أي إن التعويض في الموقع بارا (مركب D) بواسطة المجموعة الدافعة للالكترونات ($-CH_3$) يكون أكثر استقراراً مقارنة بموقعي التعويض الآخرين، بينما التعويض في الموقع ميتا (مركب F) بواسطة مجموعة ساحبة للالكترونات ($-NO_2$) يكون أكثر استقراراً، كما إن نتائج دراسة تأثير المجموعة المعوضة (مقياس الاستقرارية) كانت متوافقة تماما مع نتائج حساب حرارة التكوين. بالإضافة إلى ذلك وجد عند مقارنة قيم الكثافة الالكترونية المحسوبة لذرات النتروجين(N_7, N_8, N_{10}, N_{13}) ولكلا حالتي التعويض، إن ذرة النتروجين (N_{13}) تمتلك اقل قيمة كثافة الكترونية (قيمة شحنة أعلى)، بينما ذرة النتروجين (N_{10}) تمتلك أعلى كثافة الكترونية (قيمة شحنة اقل). إن ما تقدم من نتائج قد يعزى إلى تأثير المجموعة المعوضة من جهة، و إلى موقع التعويض من جهة اخرى.

Abstract

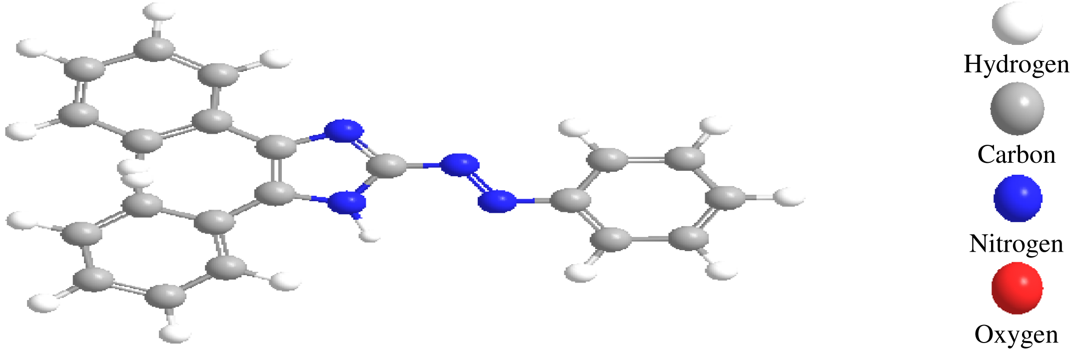
In this research, quantum mechanics calculations and using a semi-empirical methods (Parameterization 3 of MNDO model, PM3) involved the balanced geometry, for seven azo compounds (A, B, C, D, E, F, and G). The geometric dimensions (bond lengths and angles), heats of formations (ΔH_f, kcal.mol^{-1}), dipole moments (μ in Debye), orbital energies (E_{HOMO}, E_{LUMO}), ionization energies (IP, eV), a measure of stationary, (Δ, kcal.mol^{-1}) charge and the electron densities have been calculated. As show through a results that the bond length of (C-X) when ($X = CH_3, NO_2$) greater than (C-H), and the bond length of ($C-NO_2$) greater than ($C-CH_3$), and the bond length of ($N_7=N_8$) had the highest value at the position of meta, and the lowest value at the position of ortho and para in the case of substitutes ($-CH_3$) and ($-NO_2$) respectively. The calculation results showed that each of tow compound (D and F) has a lower value of heat of formation in case of substitutes ($-CH_3$,$-NO_2$), respectively, i.e., when the compensation at the position para and meta, the molecule more stability. In addition, it has been found there is compatibility between the results of heat of formation with the results of study the effect of substitutes on the stability. They also showed that the results at the comparison between the nitrogen atoms (N_7, N_8, N_{10}, N_{13}) at both the cases of compensation ($-CH_3$, $-NO_2$), found that the nitrogen atom (N_{13}) had a lower value of electron density (the highest value of the charge), In contrast, the nitrogen atom (N_{10}) had the highest value of electron density (less the value of charge). In addition, the calculation results indicate that the values of electron densities of the nitrogen atoms of the above-mentioned, is increased in compounds that have substitutes group ($-CH_3$), compared with other compounds, with the exception of nitrogen atom (N_{10}).

Key words: *Azo Imidazole Compounds, Parameterization 3 of MNDO model, PM3 N_{13},*

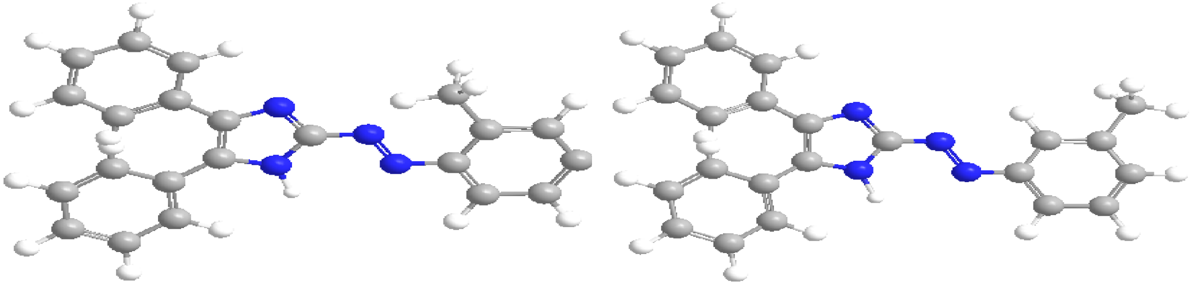
Introduction

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time [1, 2]. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium [3-5], toner [6, 7], ink-jet printing [8, 9], and oil-soluble lightfast dyes [10].

Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements, and printing systems [4, 6, and 11]. The aim of present work is to report the optimized geometries, heats of formations, dipole moments, orbital energies (HOMO, LUMO), ionization energies, charge and the electron densities for these seven azo imidazole molecules [12] (**Figure 1**) by calculation based on the PM3 model.

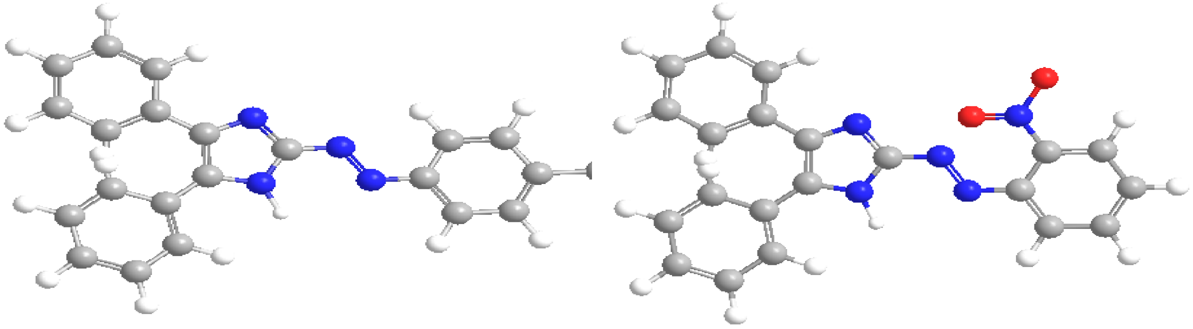


2-[Phenyl azo] – 4,5 diphenyl imidazole (A)



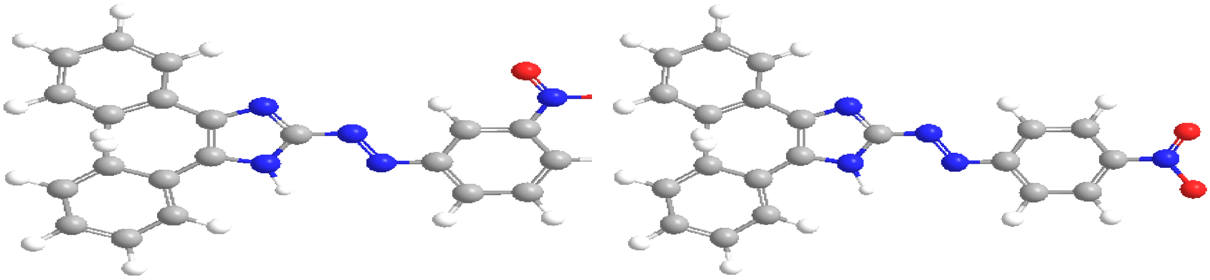
2-[(2-Methyl phenyl) azo] -4,5-diphenyl imidazole (B)

2-[(3-Methyl phenyl) azo] -4,5-diphenyl imidazole (C)



2-[(4-Methyl phenyl) azo] -4,5-diphenyl imidazole (D)

2-[(2-Nitro phenyl) azo] -4,5-diphenyl imidazole (E)



2-[(3-Nitro phenyl) azo] -4,5-diphenyl imidazole (F)

2-[(4-Nitro phenyl) azo] -4,5-diphenyl imidazole (G)

Fig. 1: (A, B, C, D, E, F, G) molecules

Geometry

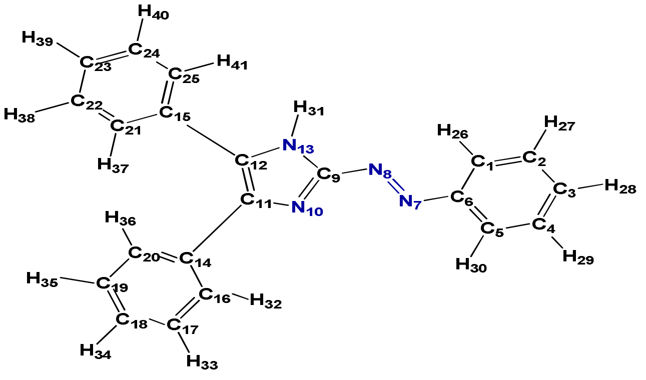
geometry (bond lengths and angles) have been studied at the balanced geometry of seven azoimidazole compounds, symbolized by the (A, B, C, D, E, F, and G). The results showed (**Table 1**) that the length of (C-X) bond when (X= CH_3 and NO_2) longer than (C-H) bond and when doing the comparison for each of the three locations of compensation (ortho, meta, and para) and for each of the two sets of compensation ($-CH_3$ and $-NO_2$), The increase in the length of (C-X) bond had a higher value in the case of substitutes for the group ($-NO_2$) compared to the other ($-CH_3$), ie, that the length of ($C-NO_2$) bond is higher than the length of ($C-CH_3$) bond when compared at each site compensation from the three sites above. also the results of this study and when a comparison for the group substitutes ($-CH_3$) in length bond (C-X) were showed the least valuable when compensation is at the location bara, while higher them the value in the site meta, either in the case of the group substitutes ($-NO_2$) that it has the least value when the compensation site para and the higher value when the compensation site ortho.

When we compare the length of bond ($N_7=N_8$) in the compound (A) with the rest of the six other compounds, it found there was an increase in the length of this bond for the six compounds, and that this increase when moving from compounds (E, F, and G) of the group substitutes ($-NO_2$) to the compounds (B, C, and D) with substitutes group ($-CH_3$) at all sites of the three above-mentioned compensation be higher value. In addition, it was clear from the results of the calculations that the length of bond ($N_7=N_8$) have the highest value in both cases of compensation ($-CH_3$ and $-NO_2$) at the site meta, while it has less value at the site ortho for the compounds in the substitutes ($-CH_3$), As for the compounds group substitutes ($-NO_2$) have the lowest value at the position of para. Also showed the results for each of the angles ($<C_6N_7N_8$ and $<N_7N_8C_9$) that the compound (A) has the highest value compared to other compounds (B-G), When follow range values of the angles above and through the results obtained from the calculation, it was found that the highest value for these angles in molecules of compensation at the site meta, except the angle ($<N_7N_8C_9$) of the molecules of the group substitutes ($-CH_3$) have the highest value at the position ortho.

The reason for all of the above may be due to the influence of the group substitutes, in terms of being a group pushing of electrons ($-CH_3$) or withdrawing of electrons ($-NO_2$), and the effect of compensation site (ortho, meta and para), on the other hand.

Table 1: Calculated geometric parameters (bond lengths in Angstrom and bond angles in degrees) of the Azo Imidazole compounds.

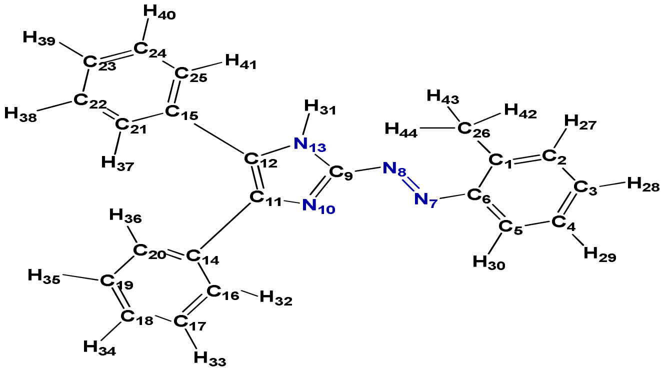
[A]



$C_1C_2=1.388$; $C_2C_3=1.392$; $C_3C_4=1.389$; $C_4C_5=1.390$; $C_5C_6=1.397$; $C_6C_1=1.404$; $C_6N_7=1.440$; $N_7N_8=1.218$; $N_8C_9=1.434$; $C_9N_{10}=1.359$; $N_{10}C_{11}=1.394$; $C_{11}C_{12}=1.401$; $C_{12}N_{13}=1.402$; $N_{13}C_9=1.393$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.457$; $C_{14}C_{16}=1.399$; $C_{16}C_{17}=1.389$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.457$; $C_{15}C_{21}=1.397$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.391$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $C_{15}C_{25}=1.397$; $C_1H_{26}=1.097$;

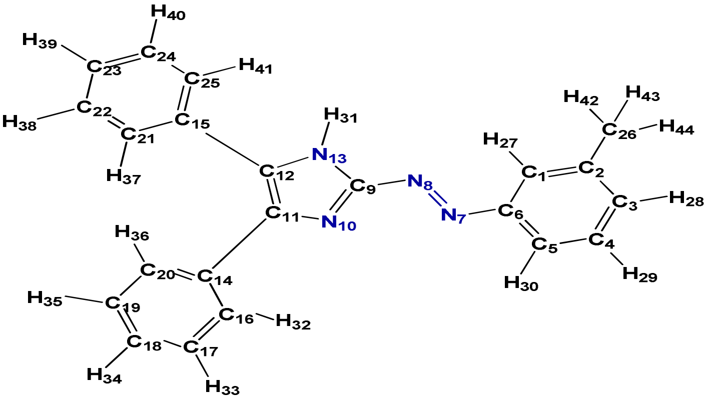
$C_2H_{27}=1.094$; $C_3H_{28}=1.094$; $C_4H_{29}=1.095$; $C_5H_{30}=1.120$; $N_{13}H_{31}=0.988$; $C_{16}H_{32}=1.097$; $C_{17}H_{33}=1.094$; $C_{18}H_{34}=1.094$; $C_{19}H_{35}=1.094$; $C_{20}H_{36}=1.097$; $C_{21}H_{37}=1.095$; $C_{22}H_{38}=1.095$; $C_{23}H_{39}=1.095$; $C_{24}H_{40}=1.095$; $C_{25}H_{41}=1.095$; $<C_6C_1C_2=119.7$; $<C_6C_1H_{26}=119.9$; $<C_1C_2C_3=120.2$; $<C_1C_2H_{27}=119.9$; $<C_2C_3C_4=119.9$; $<C_2C_3H_{28}=119.9$; $<C_3C_4C_5=120.6$; $<C_3C_4H_{29}=119.9$; $<C_4C_5C_6=119.4$; $<C_4C_5H_{30}=119.9$; $<C_5C_6C_1=120.0$; $<C_5C_6N_7=136.1$; $<C_6N_7N_8=134.1$; $<N_7N_8C_9=131.3$; $<N_8C_9N_{10}=132.1$; $<N_{10}C_9N_{13}=108.2$; $<C_9N_{10}C_{11}=108.7$; $<N_{10}C_{11}C_{12}=111.0$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=119.9$; $<C_{12}N_{13}C_9=108.5$; $<C_{12}N_{13}H_{31}=121.6$.

[B]



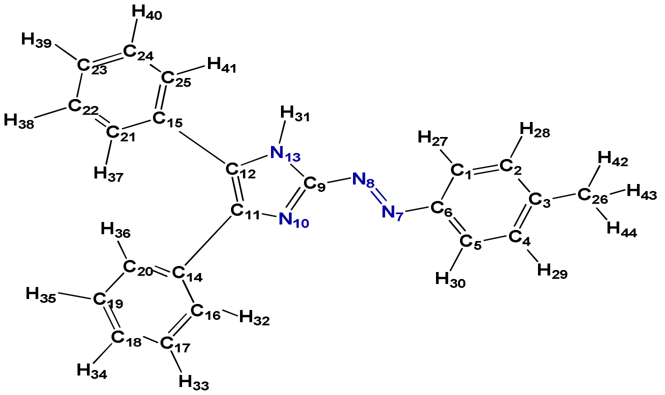
$C_1C_2=1.397$; $C_2C_3=1.389$; $C_3C_4=1.390$; $C_4C_5=1.388$; $C_5C_6=1.399$; $C_6C_1=1.406$; $C_6N_7=1.445$; $N_7N_8=1.230$; $N_8C_9=1.430$; $C_9N_{10}=1.356$; $N_{10}C_{11}=1.394$; $C_{11}C_{12}=1.400$; $C_{12}N_{13}=1.401$; $N_{13}C_9=1.398$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.459$; $C_{14}C_{16}=1.399$; $C_{16}C_{17}=1.390$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.398$; $C_{15}C_{21}=1.396$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.390$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $C_{15}C_{25}=1.396$; $C_1C_{26}=1.486$; $C_2H_{27}=1.096$; $C_3H_{28}=1.095$; $C_4H_{29}=1.094$; $C_5H_{30}=1.096$; $N_{13}H_{31}=0.987$; $C_{16}H_{32}=1.096$; $C_{17}H_{33}=1.094$; $C_{18}H_{34}=1.094$; $C_{19}H_{35}=1.094$; $C_{20}H_{36}=1.097$; $C_{21}H_{37}=1.095$; $C_{22}H_{38}=1.095$; $C_{23}H_{39}=1.095$; $C_{24}H_{40}=1.095$; $C_{25}H_{41}=1.095$; $C_{26}H_{42}=1.098$; $C_{26}H_{43}=1.098$; $C_{26}H_{44}=1.098$; $<C_6C_1C_2=118.5$; $<C_6C_1C_{26}=122.1$; $<C_1C_2C_3=120.8$; $<C_1C_2H_{27}=119.9$; $<C_2C_3C_4=120.0$; $<C_2C_3H_{28}=119.9$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{29}=119.9$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{30}=119.9$; $<C_5C_6C_1=120.4$; $<C_5C_6N_7=122.2$; $<C_6N_7N_8=119.7$; $<N_7N_8C_9=119.6$; $<N_8C_9N_{10}=130.8$; $<N_{10}C_9N_{13}=108.7$; $<C_9N_{10}C_{11}=108.3$; $<N_{10}C_{11}C_{12}=111.0$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=119.9$; $<C_{12}N_{13}C_9=108.0$; $<C_{12}N_{13}H_{31}=124.4$.

[C]



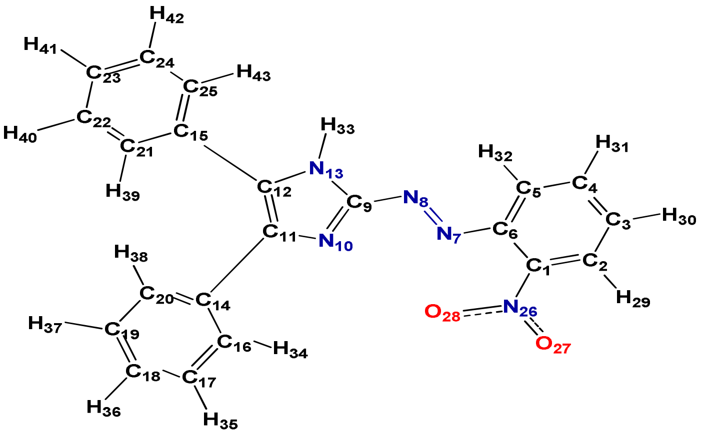
$C_1C_2=1.419$; $C_2C_3=1.419$; $C_3C_4=1.419$; $C_4C_5=1.4199$; $C_5C_6=1.419$; $C_6C_1=1.419$; $C_6N_7=1.358$; $N_7N_8=1.332$; $N_8C_9=1.357$; $C_9N_{10}=1.357$; $N_{10}C_{11}=1.357$; $C_{11}C_{12}=1.419$; $C_{12}N_{13}=1.317$; $N_{13}C_9=1.461$; $C_{11}C_{14}=1.419$; $C_{12}C_{15}=1.419$; $C_{14}C_{16}=1.419$; $C_{16}C_{17}=1.419$; $C_{17}C_{18}=1.419$; $C_{18}C_{19}=1.419$; $C_{19}C_{20}=1.420$; $C_{14}C_{20}=1.419$; $C_{15}C_{21}=1.419$; $C_{21}C_{22}=1.419$; $C_{22}C_{23}=1.419$; $C_{23}C_{24}=1.419$; $C_{24}C_{25}=1.419$; $C_{15}C_{25}=1.419$; $C_1H_{27}=1.099$; $C_2C_{26}=1.496$; $C_3H_{28}=1.099$; $C_4H_{29}=1.099$; $C_5H_{30}=1.099$; $N_{13}H_{31}=1.049$; $C_{16}H_{32}=1.100$; $C_{17}H_{33}=1.099$; $C_{18}H_{34}=1.099$; $C_{19}H_{35}=1.099$; $C_{20}H_{36}=1.099$; $C_{21}H_{37}=1.099$; $C_{22}H_{38}=1.099$; $C_{23}H_{39}=1.099$; $C_{24}H_{40}=1.099$; $C_{25}H_{41}=1.100$; $C_{26}H_{42}=1.112$; $C_{26}H_{43}=1.112$; $C_{26}H_{44}=1.112$; $<C_6C_1C_2=119.6$; $<C_6C_1H_{27}=119.9$; $<C_1C_2C_3=119.819$; $<C_1C_2C_{26}=120.5$; $<C_2C_3C_4=120.3$; $<C_2C_3H_{28}=119.9$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{29}=119.9$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{30}=119.9$; $<C_5C_6C_1=120.4$; $<C_5C_6N_7=115.1$; $<C_6N_7N_8=120.0$; $<N_7N_8C_9=119.7$; $<N_8C_9N_{10}=130.9$; $<N_{10}C_9N_{13}=108.6$; $<C_9N_{10}C_{11}=108.2$; $<N_{10}C_{11}C_{12}=111.0$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=120.0$; $<C_{12}N_{13}C_9=108.1$; $<C_{12}N_{13}H_{31}=124.3$.

[D]



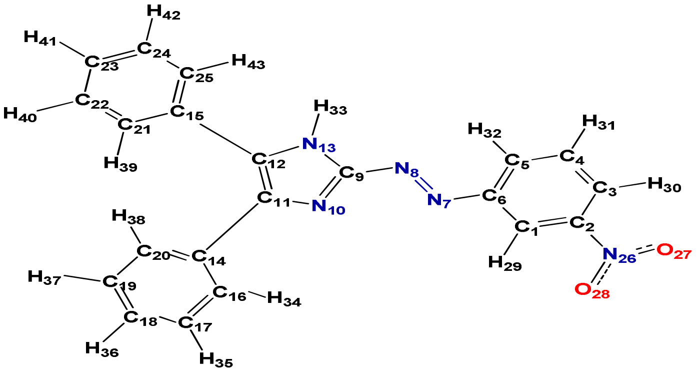
$C_1C_2=1.389$; $C_2C_3=1.3952$; $C_3C_4=1.397$; $C_4C_5=1.387$; $C_5C_6=1.402$; $C_6C_1=1.399$; $C_6N_7=1.443609$; $N_7N_8=1.231$; $N_8C_9=$ 1.430; $C_9N_{10}=1.357$; $N_{10}C_{11}=1.393$; $C_{11}C_{12}=1.402$; $C_{12}N_{13}=1.402$; $N_{13}C_9=1.397$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.456$; $C_{14}C_{16}=1.398$; $C_{16}C_{17}=1.390$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.398$; $C_{15}C_{21}=1.397$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.391$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $C_{15}C_{25}=1.397$; $C_1H_{27}=1.096$; $C_2H_{28}=1.096$; $C_3C_{26}=1.485$; $C_4H_{29}=1.095$; $C_5H_{30}=1.097$; $N_{13}H_{31}=0.988$; $C_{16}H_{32}=1.096$; $C_{17}H_{33}=1.094$; $C_{18}H_{34}=1.094$; $C_{19}H_{35}=1.094$; $C_{20}H_{36}=1.096$; $C_{21}H_{37}=1.096$; $C_{22}H_{38}=1.095$; $C_{23}H_{39}=1.094$; $C_{24}H_{40}=1.094$; $C_{25}H_{41}=1.095$; $C_{26}H_{42}=1.098$; $C_{26}H_{43}=1.098$; $C_{26}H_{44}=1.097$; $<C_6C_1C_2=119.9$; $<C_6C_1H_{27}=119.9$; $<C_1C_2C_3=119.9$; $<C_1C_2H_{28}=120.0$; $<C_2C_3C_4=119.9$; $<C_2C_3C_{26}=119.9$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{29}=120.0$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{30}=119.9$; $<C_5C_6C_1=120.0$; $<C_5C_6N_7=120.0$; $<C_6N_7N_8=107.4$; $<N_7N_8C_9=107.4$; $<N_8C_9N_{10}=121.5$; $<N_{10}C_9N_{13}=110.9$; $<C_9N_{10}C_{11}=104.5$; $<N_{10}C_{11}C_{12}=110.9$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=119.9$; $<C_{12}N_{13}C_9=104.9$; $<C_{12}N_{13}H_{31}=127.5$.

[E]



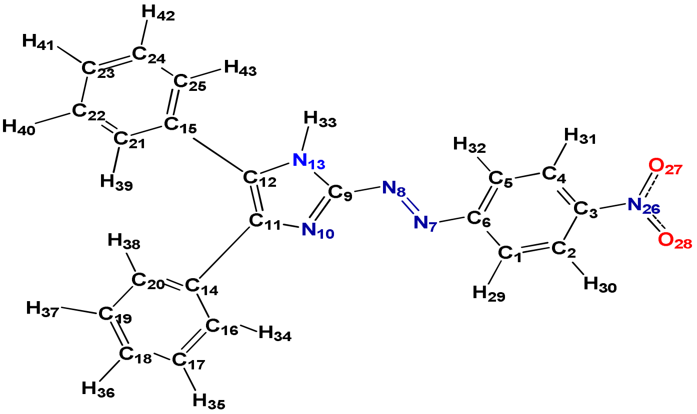
$C_1C_2=1.399$; $C_2C_3=1.387$; $C_3C_4=1.391$; $C_4C_5=1.388$; $C_5C_6=1.401$; $C_6C_1=1.404$; $C_6N_7=1.449$; $N_7N_8=1.229$; $N_8C_9=1.425$; $C_9N_{10}=1.359$; $N_{10}C_{11}=1.391$; $C_{11}C_{12}=1.403$; $C_{12}N_{13}=1.398$; $N_{13}C_9=1.399$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.459$; $C_{14}C_{16}=1.398$; $C_{16}C_{17}=1.390$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.398$; $C_{15}C_{21}=1.396$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.390$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $N_{26}O_{27}=1.213$; $N_{26}O_{28}=1.213$; $C_{15}C_{25}=1.396$; $C_1N_{26}=1.503$; $C_2H_{29}=1.098$; $C_3H_{30}=1.095$; $C_4H_{31}=1.095$; $C_5H_{32}=1.098$; $N_{13}H_{33}=0.987$; $C_{16}H_{34}=1.096$; $C_{17}H_{35}=1.094$; $C_{18}H_{36}=1.094$; $C_{19}H_{37}=1.094$; $C_{20}H_{38}=1.097$; $C_{21}H_{39}=1.095$; $C_{22}H_{40}=1.095$; $C_{23}H_{41}=1.095$; $C_{24}H_{42}=1.095$; $C_{25}H_{43}=1.095$; $<C_6C_1C_2=119.4$; $<C_6C_1N_{26}=123.1$; $<C_1C_2C_3=120.3$; $<C_1C_2H_{29}=119.9$; $<C_2C_3C_4=119.9$; $<C_2C_3H_{30}=119.9$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{31}=119.9$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{32}=119.9$; $<C_5C_6C_1=119.7$; $<C_5C_6N_7=114.5$; $<C_6N_7N_8=119.6$; $<N_7N_8C_9=120.6$; $<N_8C_9N_{10}=130.2$; $<N_{10}C_9N_{13}=108.7$; $<C_9N_{10}C_{11}=108.2$; $<N_{10}C_{11}C_{12}=111.0$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=120.0$; $<C_{12}N_{13}C_9=107.9$; $<C_{12}N_{13}H_{33}=124.5$.

[F]



$C_1C_2=1.399$; $C_2C_3=1.400$; $C_3C_4=1.389$; $C_4C_5=1.389$; $C_5C_6=1.402$; $C_6C_1=1.397$; $C_6N_7=1.447$; $N_7N_8=1.231$; $N_8C_9=1.426$; $C_9N_{10}=1.358$; $N_{10}C_{11}=1.390$; $C_{11}C_{12}=1.403$; $C_{12}N_{13}=1.400$; $N_{13}C_9=1.398$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.456$; $C_{14}C_{16}=1.398$; $C_{16}C_{17}=1.390$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.398$; $C_{15}C_{21}=1.397$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.391$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $N_{26}O_{27}=1.215$; $N_{26}O_{28}=1.214$; $C_{15}C_{25}=1.398$; $C_1H_{29}=1.101$; $C_2N_{26}=1.498$; $C_3H_{30}=1.099$; $C_4H_{31}=1.096$; $C_5H_{32}=1.098$; $N_{13}H_{33}=0.988$; $C_{16}H_{34}=1.096$; $C_{17}H_{35}=1.094$; $C_{18}H_{36}=1.094$; $C_{19}H_{37}=1.094$; $C_{20}H_{38}=1.096$; $C_{21}H_{39}=1.096$; $C_{22}H_{40}=1.095$; $C_{23}H_{41}=1.094$; $C_{24}H_{42}=1.095$; $C_{25}H_{43}=1.095$; $<C_6C_1C_2=119.3$; $<C_6C_1H_{29}=119.9$; $<C_1C_2C_3=120.1$; $<C_1C_2N_{26}=119.9$; $<C_2C_3C_4=119.8$; $<C_2C_3H_{30}=108.6$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{31}=108.6$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{32}=108.6$; $<C_5C_6C_1=120.5$; $<C_5C_6N_7=114.9$; $<C_6N_7N_8=119.7$; $<N_7N_8C_9=120.1$; $<N_8C_9N_{10}=130.6$; $<N_{10}C_9N_{13}=108.6$; $<C_9N_{10}C_{11}=108.2$; $<N_{10}C_{11}C_{12}=100.7$; $<N_{10}C_{11}C_{14}=152.9$; $<C_{11}C_{12}N_{13}=99.7$; $<C_{11}C_{12}C_{15}=104.3$; $<C_{12}N_{13}C_9=108.1$; $<C_{12}N_{13}H_{33}=138.5$.

[G]



$C_1C_2=1.388$; $C_2C_3=1.400$; $C_3C_4=1.400$; $C_4C_5=1.387$; $C_5C_6=1.398$; $C_6C_1=1.398$; $C_6N_7=1.446$; $N_7N_8=1.227$; $N_8C_9=1.428$; $C_9N_{10}=1.358$; $N_{10}C_{11}=1.391$; $C_{11}C_{12}=1.402$; $C_{12}N_{13}=1.398$; $N_{13}C_9=1.399$; $C_{11}C_{14}=1.457$; $C_{12}C_{15}=1.459$; $C_{14}C_{16}=1.398$; $C_{16}C_{17}=1.390$; $C_{17}C_{18}=1.390$; $C_{18}C_{19}=1.390$; $C_{19}C_{20}=1.389$; $C_{14}C_{20}=1.398$; $C_{15}C_{21}=1.396$; $C_{21}C_{22}=1.390$; $C_{22}C_{23}=1.390$; $C_{23}C_{24}=1.391$; $C_{24}C_{25}=1.390$; $N_{26}O_{27}=1.215$; $N_{26}O_{28}=1.215$; $C_{15}C_{25}=1.396$; $C_1H_{29}=1.096$; $C_2H_{30}=1.099$; $C_3N_{26}=1.496$; $C_4H_{31}=1.099$; $C_5H_{32}=1.096$; $N_{13}H_{33}=0.987$; $C_{16}H_{34}=1.096$; $C_{17}H_{35}=1.094$; $C_{18}H_{36}=1.094$; $C_{19}H_{37}=1.094$; $C_{20}H_{38}=1.097$; $C_{21}H_{39}=1.095$; $C_{22}H_{40}=1.095$; $C_{23}H_{41}=1.095$; $C_{24}H_{42}=1.095$; $C_{25}H_{43}=1.095$; $<C_6C_1C_2=119.9$; $<C_6C_1H_{29}=108.6$; $<C_1C_2C_3=119.9$; $<C_1C_2H_{30}=108.6$; $<C_2C_3C_4=119.9$; $<C_2C_3N_{26}=119.9$; $<C_3C_4C_5=119.9$; $<C_3C_4H_{31}=120.0$; $<C_4C_5C_6=120.0$; $<C_4C_5H_{32}=119.9$; $<C_5C_6C_1=120.0$; $<C_5C_6N_7=119.9$; $<C_6N_7N_8=107.5$; $<N_7N_8C_9=107.4$; $<N_8C_9N_{10}=121.5$; $<N_{10}C_9N_{13}=110.9$; $<C_9N_{10}C_{11}=104.5$; $<N_{10}C_{11}C_{12}=111.0$; $<N_{10}C_{11}C_{14}=124.5$; $<C_{11}C_{12}N_{13}=108.4$; $<C_{11}C_{12}C_{15}=120.0$; $<C_{12}N_{13}C_9=104.9$; $<C_{12}N_{13}H_{33}=141.6$.

Physical Characteristics

This research involved study of some physical properties ; heats of formation (ΔH_f, *kcal.mol*$^{-}$), Dipole moments (μ *in Debye*), energies (*IP, eV*) of the High Occupied Molecular Orbital (E_{HOMO}) and the Lower Unoccupied Molecular Orbital (E_{LUMO}) and according to Koopmans' theorem (the negative E_{HOMO} is equal to the ionization potential) the calculation has been ionization energies (*IP, eV*).

The results showed (**Table 2**), and by follow-up the values of heat of formation of the compounds studied, it has been found in the case of molecules with the group substitutes ($-CH_3$), the compound (D) be the lower value, while the compound (B) have a higher value, and this means that the molecule in which compensation on-site para (compound-D) is more stable, and have the compound (B) on the contrary. While the results showed when comparing molecules of the group substitutes ($-NO_2$) be the compound (F) has a lower value of heat of formation, either the compound (E) have a higher value, meaning that the compound which compensation at the site meta (compound-F) is more stable compared with other two sites, and be on the contrary in the case of compensation in the ortho site (compound-E). This may be due cause, the effect location of compensation for each group, which gives the molecule of resonance more in case of compensation for the group driving the electrons ($-CH_3$) at the position of para and ortho compared with the location meta, the other hand, high-impact for disability stereochemistry at compensation in location ortho compared with the location para. As in the case of electron withdrawing group ($-NO_2$), it give more cases of resonance at the position of meta compared with other two sites. In addition, the results have shown that such compensators and compensation to all the locations, they increase the value of the Dipole moments, except for compound (E). It was found that the compound which have the highest value for (E_{HOMO}) is compounds (D) and (E) in the case of group substitutes ($-CH_3$) and ($-NO_2$), respectively, so both of the molecule (A and D) were the most tendency to lose electrons. While the compound that has the lowest value (E_{LUMO}) is compound (B) and compound (G) in the case of group substitutes ($-CH_3$) and ($-NO_2$), respectively, so both of the compound (B and G) were the most tendency to gain electrons. The study showed that both of the compound (D and E) that have the substitutes ($-CH_3$) and ($-NO_2$), respectively, have a value less of ionization potential, so they have been ionization easier. This may be due to the same reason mentioned previously.

Table 2: Calculated heats of formation (in kcal/mole), dipole moments (in Debye), orbital energies (E_{HOMO}, E_{LUMO}, in eV) and ionization energies (IP, in eV) for Azo Imidazole compounds

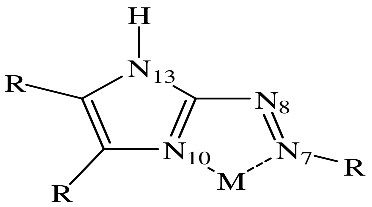
Molecules	ΔH_f (kcal/mole)	Dipole moment (μ in Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	IP (eV)
A	147.910	2.880	-8.779	0.843	8.779
B	138.586	3.554	-8.668	0.763	8.667
C	137.048	3.852	-8.605	0.895	8.604
D	136.837	3.649	-8.585	0.900	8.585
E	141.495	2.272	-8.819	1.344	8.818
F	138.125	3.134	-8.827	1.458	8.826
G	138.169	7.646	-8.984	1.247	8.983

Charges and Electronic densities

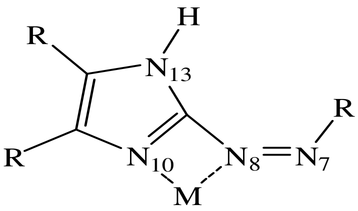
In this study, charges and electronic densities has been calculate for all atoms in the molecules studied (**Table 3**). It was found when comparing compounds (B, C, and D) for the substitutes ($-CH_3$) and each atom of nitrogen (N_7, N_8, N_{10}, N_{13}), the compound (B) has a lower value of electron density (the highest value of the charge) with the exception of an atom of nitrogen (N_{10}), while the compound (D) on mostly has the highest value of electron density (less the value of the charge). As in the case of compounds (E, F, G) for the group substitutes ($-NO_2$), it was found that the compound (G) has a lower value of electron density (the highest value of the charge), except for an atom of nitrogen (N_{13}), either the compound (F), it has the highest value of the electron density (less the value of the charge).

Also when we compared between the nitrogen atoms of the above at both the cases of compensation (-CH_3 and -NO_2), found that the nitrogen atom (N_{13}) has a lower value of electron density (the highest value of the charge), while the nitrogen atom (N_{10}) be the opposite of that, Where had the highest value of electron density (less the value of charge). In addition, the calculation results indicate that the values of electron density of the nitrogen atoms of the above-mentioned, is increased when compounds that have substitutes group (-CH_3), compared with other compounds, with the exception of nitrogen atom (N_{10}).

These compounds studied when behave as molecules coordinates (the composition of complexes), they are associated with the metal from two position (bidintate), and the atoms donor of electrons in the molecules studied are the atoms of nitrogen, so we can conclude that the atom of nitrogen (N_{10}), is one of the sites link with the metal, and for being has the highest density of electronic compared with other atoms. Also excluded atom of nitrogen (N_{13}) of the link, because of its association with a hydrogen atom, so it is expected to be the link other from an atom of nitrogen (N_7), and not (N_8), because in the first case (with atom N_7) will be form the configure link pentaring, which is more stable than the tetraring, formed by the link at nitrogen atom (N_8), and because of effect of high stereochemistry block.



More stability



Less stability

Also the conclusion described above supported by the practical study by the researcher H. A. Abdul Hussein [12].

Table 3: Calculated charge and electron densities for outer shell atoms of the Azo Imidazole compounds (See Table 1 for numbering)

Atom	A	B	C	D
	Charge (Electron density)	Charge (Electron density)	Charge (Electron density)	Charge (Electron density)
C_1	-0.0463 (4.0463)	-0.0224 (4.0224)	-0.0795 (4.0795)	-0.0719 (4.0719)
C_2	-0.1244 (4.1245)	-0.1151 (4.1151)	-0.0829 (4.0830)	-0.1141 (4.1142)
C_3	-0.0770 (4.0771)	-0.0824 (4.0825)	-0.0836 (4.0836)	-0.0503(4.0504)
C_4	-0.1071 (4.1072)	-0.1141 (4.1142)	-0.1099 (4.1099)	-0.1196 (4.1197)
C_5	-0.1305 (4.1305)	-0.0811 (4.0811)	-0.0539 (4.0540)	-0.0419 (4.0420)
C_6	-0.1262 (4.1262)	-0.0902 (4.0903)	-0.0921 (4.0921)	-0.1042 (4.1042)
N_7	0.0573 (4.9427)	0.0378 (4.9621)	0.0326 (4.9673)	0.0350 (4.9649)
N_8	0.0120 (4.9879)	-0.0092 (5.0092)	-0.0145 (5.0145)	-0.0171 (5.0171)
C_9	-0.2686 (4.2687)	-0.2450 (4.2451)	-0.2391 (4.2391)	-0.2379 (4.2379)
N_{10}	-0.1037 (5.1037)	-0.0645 (5.0646)	-0.0627 (5.0627)	-0.0636 (5.0636)
C_{11}	-0.0452 (4.0453)	-0.0551 (4.0551)	-0.0564 (4.0565)	-0.0564 (4.0565)
C_{12}	-0.2367 (4.2368)	-0.2370 (4.2371)	-0.2332 (4.2333)	-0.2336 (4.2337)
N_{13}	0.3936 (4.6063)	0.3712 (4.6287)	0.3667 (4.6332)	0.3664 (4.6336)
C_{14}	-0.0054 (4.0054)	-0.0005 (4.0005)	-0.0030 (4.0030)	-0.0028 (4.0028)
C_{15}	-0.0204 (4.0204)	-0.0196 (4.0197)	-0.0129 (4.0129)	-0.0126 (4.0127)
C_{16}	-0.0786 (4.0786)	-0.0736 (4.0736)	-0.0729 (4.0729)	-0.0729 (4.0730)
C_{17}	-0.1075 (4.1075)	-0.1091 (4.1091)	-0.1091 (4.1091)	-0.1092 (4.1092)
C_{18}	-0.0988 (4.0989)	-0.1019 (4.1020)	-0.1016 (4.1017)	-0.1017 (4.1018)
C_{19}	-0.1045 (4.1046)	-0.1066 (4.1066)	-0.1073 (4.1074)	-0.1073 (4.1074)
C_{20}	-0.0989 (4.0990)	-0.1041 (4.1042)	-0.0998 (4.0999)	-0.1000 (4.1000)
C_{21}	-0.0766 (4.0767)	-0.0782 (4.0783)	-0.0779 (4.0780)	-0.0780 (4.0781)
C_{22}	-0.1009 (4.1009)	-0.1021 (4.1022)	-0.0995 (4.0995)	-0.0995 (4.0996)

C_{23}	-0.0919 (4.0920)	-0.0914 (4.0914)	-0.0955 (4.0955)	-0.0956 (4.0957)
C_{24}	-0.1007 (4.1008)	-0.1037 (4.1038)	-0.1001 (4.1001)	-0.1001 (4.1001)
C_{25}	-0.0955 (4.0956)	-0.0886 (4.0886)	-0.1023 (4.1024)	-0.1023 (4.1024)
$H_{26}(C_{26})$	0.1160 (0.8839)	-0.0723 (4.0723)	-0.0649 (4.0649)	-0.0699 (4.0699)
H_{27}	0.1056 (0.8943)	0.1096 (0.8903)	0.1197 (0.8802)	0.1159 (0.8841)
H_{28}	0.1017 (0.8983)	0.1035 (0.8964)	0.1063 (0.8937)	0.1091 (0.8909)
H_{29}	0.1048 (0.8951)	0.1059 (0.8941)	0.1069 (0.8931)	0.1098 (0.8902)
H_{30}	0.1854 (0.8145)	0.1134 (0.8866)	0.1222 (0.8778)	0.1213 (0.8786)
H_{31}	0.0831 (0.9168)	0.0800 (0.9199)	0.0800 (0.9200)	0.0800 (0.9199)
H_{32}	0.1172 (0.8827)	0.1215 (0.8784)	0.1207 (0.8793)	0.1207 (0.8792)
H_{33}	0.1029 (0.8970)	0.1021 (0.8978)	0.1024 (0.8976)	0.1023 (0.8976)
H_{34}	0.1022 (0.8977)	0.1007 (0.8993)	0.1009 (0.8991)	0.1009 (0.8991)
H_{35}	0.1028 (0.8971)	0.1008 (0.8992)	0.1015 (0.8985)	0.1014 (0.8985)
H_{36}	0.1150 (0.8849)	0.1133 (0.8867)	0.1122 (0.8877)	0.1123 (0.8877)
H_{37}	0.1168 (0.8831)	0.1131 (0.8868)	0.1189 (0.8810)	0.1189 (0.8811)
H_{38}	0.1076 (0.8924)	0.1067 (0.8932)	0.1069 (0.8931)	0.1068 (0.8931)
H_{39}	0.1059 (0.8940)	0.1052 (0.8947)	0.1052 (0.8948)	0.1051 (0.8948)
H_{40}	0.1069 (0.8930)	0.1065 (0.8934)	0.1054 (0.8946)	0.1054 (0.8946)
H_{41}	0.1086 (0.8913)	0.1124 (0.8875)	0.1054 (0.8946)	0.1054 (0.8945)
H_{42}	----------------------	0.0425 (0.9574)	0.0480 (0.9520)	0.0501 (0.9498)
H_{43}	----------------------	0.0686 (0.9314)	0.0482 (0.9518)	0.0503 (0.9496)
H_{44}	----------------------	0.0529 (0.9470)	0.0446 (0.9553)	0.0456 (0.9543)

Table 4: Calculated charge and electron densities for outer shell atoms of the Azo Imidazole compounds (See Table 1 for numbering)

Atom	**A**	**E**	**F**	**G**
	Charge (Electron density)	Charge (Electron density)	Charge (Electron density)	Charge (Electron density)
C_1	-0.0463 (4.0463)	-0.3718 (4.3719)	0.0062 (3.9938)	-0.1256 (4.1257)
C_2	-0.1244 (4.1245)	-0.0294 (4.0295)	-0.4160 (4.4160)	0.0048 (3.9952)
C_3	-0.0770 (4.0771)	-0.1049 (4.1049)	0.0065 (3.9935)	-0.4214 (4.4214)
C_4	-0.1071 (4.1072)	-0.0553 (4.0554)	-0.1343 (4.1344)	0.0041 (3.9959)
C_5	-0.1305 (4.1305)	-0.0815 (4.0816)	0.0070 (3.9930)	-0.1213 (4.1214)
C_6	-0.1262 (4.1262)	0.0077 (3.9922)	-0.1083 (4.1084)	0.0001 (3.9999)
N_7	0.0573 (4.9427)	0.0183 (4.9817)	0.0170 (4.9830)	0.0262 (4.9738)
N_8	0.0120 (4.9879)	0.0209 (4.9791)	0.0100 (4.9899)	0.0292 (4.9707)
C_9	-0.2686 (4.2687)	-0.2599 (4.2600)	-0.2554 (4.2555)	-0.2713 (4.2714)
N_{10}	-0.1037 (5.1037)	-0.0535 (5.0536)	-0.0546 (5.0546)	-0.0511 (5.0512)
C_{11}	-0.0452 (4.0453)	-0.0556 (4.0556)	-0.0572 (4.0572)	-0.0530 (4.0531)
C_{12}	-0.2367 (4.2368)	-0.2261 (4.2262)	-0.2234 (4.2234)	-0.2266 (4.2266)
N_{13}	0.3936 (4.6063)	0.3899 (4.6101)	0.3767 (4.6233)	0.3830 (4.6169)
C_{14}	-0.0054 (4.0054)	-0.0035 (4.0036)	-0.0064 (4.0065)	-0.0064 (4.0065)
C_{15}	-0.0204 (4.0204)	-0.0264 (4.0264)	-0.0189 (4.0190)	-0.0274 (4.0275)
C_{16}	-0.0786 (4.0786)	-0.0725 (4.0725)	-0.0727 (4.0728)	-0.0721 (4.0721)
C_{17}	-0.1075 (4.1075)	-0.1087 (4.1088)	-0.1085 (4.1086)	-0.1080 (4.1080)
C_{18}	-0.0988 (4.0989)	-0.1001 (4.1002)	-0.0993 (4.0994)	-0.0982 (4.0983)
C_{19}	-0.1045 (4.1046)	-0.1061 (4.1062)	-0.1064 (4.1064)	-0.1057 (4.1057)
C_{20}	-0.0989 (4.0990)	-0.1022 (4.1023)	-0.0973 (4.0973)	-0.1015 (4.1015)
C_{21}	-0.0766 (4.0767)	-0.0746 (4.0746)	-0.0764 (4.0764)	-0.0760 (4.0761)
C_{22}	-0.1009 (4.1009)	-0.1009 (4.1010)	-0.0988 (4.0988)	-0.1009 (4.1009)
C_{23}	-0.0919 (4.0920)	-0.0890 (4.0891)	-0.0926 (4.0927)	-0.0882 (4.0882)
C_{24}	-0.1007 (4.1008)	-0.1035 (4.1036)	-0.0986 (4.0987)	-0.1025 (4.1025)
C_{25}	-0.0955 (4.0956)	-0.0875 (4.0876)	-0.1010 (4.1010)	-0.0878 (4.0878)
$H_{26}(N_{26})$	0.1160 (0.8839)	1.3096 (3.6903)	1.3073 (3.6926)	1.3090 (3.6909)
$H_{27}(O_{27})$	0.1056 (0.8943)	-0.5911 (6.5912)	-0.5991 (6.5992)	-0.6000 (6.6001)
$H_{28}(O_{28})$	0.1017 (0.8983)	-0.5923 (6.5923)	-0.5971 (6.5972)	-0.6003 (6.6003)
H_{29}	0.1048 (0.8951)	0.1215 (0.8784)	0.1457 (0.8542)	0.1245 (0.8754)
H_{30}	0.1854 (0.8145)	0.1156 (0.8843)	0.1340 (0.8659)	0.1340 (0.8659)
H_{31}	0.0831 (0.9168)	0.1117 (0.8883)	0.1192 (0.8807)	0.1341 (0.8659)
H_{32}	0.1172 (0.8827)	0.1311 (0.8688)	0.1273 (0.8727)	0.1261 (0.8739)

H_{33}	0.1029 (0.8970)	0.0844 (0.9156)	0.0823 (0.9177)	0.0812 (0.9188)
H_{34}	0.1022 (0.8977)	0.1211 (0.8789)	0.1189 (0.8810)	0.1205 (0.8795)
H_{35}	0.1028 (0.8971)	0.1026 (0.8973)	0.1030 (0.8969)	0.1035 (0.8965)
H_{36}	0.1150 (0.8849)	0.1011 (0.8988)	0.1018 (0.8981)	0.1020 (0.8980)
H_{37}	0.1168 (0.8831)	0.1014 (0.8985)	0.1026 (0.8974)	0.1021 (0.8978)
H_{38}	0.1076 (0.8924)	0.1133 (0.8866)	0.1122 (0.8878)	0.1131 (0.8869)
H_{39}	0.1059 (0.8940)	0.1146 (0.8853)	0.1190 (0.8810)	0.1134 (0.8866)
H_{40}	0.1069 (0.8930)	0.1078 (0.8922)	0.1077 (0.8923)	0.1081 (0.8918)
H_{41}	0.1086 (0.8913)	0.1056 (0.8944)	0.1061 (0.8938)	0.1065 (0.8934)
H_{42}	-----------------------	0.1069 (0.8931)	0.1067 (0.8933)	0.1078 (0.8921)
H_{43}	-----------------------	0.1116 (0.8883)	0.1051 (0.8948)	0.1119 (0.8880)

Effect the compensators on stability

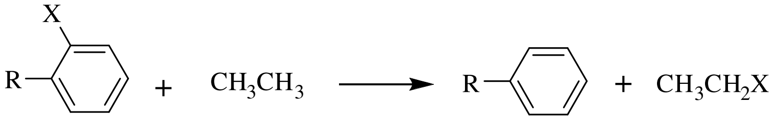
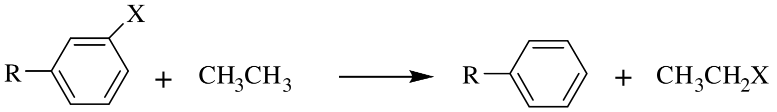
The study of effect of substitutes on stability (a measure of stationary, Δ) depending on the heats of formation reactive material and the product, were carried out according to Isodesmic Reaction [13]. Isodesmic reactions represent a subclass of isogyric reactions, the latter of which are defined as transformations in which reactants and products have the same number of electron pairs. These reactions can, in principle, be purely hypothetical and can also be used to quantify the stability of reactive intermediates in a thermochemical sense, in the sense, it is a chemical reaction in which the type of chemical bonds broken in the reactant are the same as the type of bonds formed in the reaction product. This type of reaction is often used as a hypothetical reaction in thermochemistry. Where,

$$\Delta = (H\Delta_f)_{product} - (H\Delta_f)_{react}$$

When we notice results in the Table 5 found both (D and F) has the highest value for (Δ). This indicates that the group substitutes (-CH$_3$) on-site para (compound- D) increase in stability, compared with (B and C) of others, while substitutes group (-NO$_2$) in the site meta (compound-F) increase in stability, compared with (G and E) of others, since when the value (Δ) was the highest value, the compensator will increase the Stationary clearly. This may be due to the same reason stated previously. The results also show that the lowest value (Δ) at the position of ortho. It may be because high spatial impact of Impeding.

And this can be conclude, where the calculation results indicate that the sequence of values (Δ) be the exact opposite of the sequence of values of heats of formation of all molecules studied, and this shows the role of the substitutes group in stability the compound.

Table 5: Evaluation of substituted effects using PM3 calculations (energies Δ , in kcal/mol)

Isodesmic Reaction	X=-CH$_3$	X=-NO$_2$
	-B- 3.822	-E- 3.112
	-C- 5.360	-F- 6.482
	-D- 5.571	-G- 6.438

Where; X= CH$_3$, NO$_2$, R = C$_{15}$H$_{11}$N$_4$

References

1) Kilincarslan R, Erdem E, and Kocaokutgen H. *Transition Metal Chemistry.* **(2007)**, 32, 102-106.

2) Chung Y and Chen C. *Chem. Lett.* **(2009)**, 7,347-352.

3) Prime R, Chiou G, and Twieg R. *Journal of Thermal Analysis.* **(1996),** 46, 1133-1150.

4) Reinke N, Draude A, Fuhrmann T, Franke H, and Lessard R A. *Applied Physics B*. **(2004),** 78, 205-209.

5) Tong X, Wang G, Soldera A, and Zhao Y. *Journal of Physics Chemistry B.* **(2005)**, 109, 20281-20393.

6) Ivanov V M and Kochelaeva G A. *Journal of Analytical Chemistry. (***2003),** 58, 1, 31–37.

7) Prithwiraj B. *Transition Metal Chemistry.* **(2005)**, 30:978–986.

8) Hurduc N, Enea R, Resmerita A M, Moleavin I, Cristea M, and Scutaru D. *Journal of Polymaterial Scinice: Part A: Polymaterial Chemistry***. (2008),** 44, 65-83.

9) Gregory P, Waring D R, and Hallos G. The Chemistry and Application of Dyes**.** Plenum Press, London. **(1990),** 18-20.

10) Bobrovsky A, Shibaev V, Hamplova V, Kaspar M, and Glogarova M. *Colloidal Polymer Science***. (2010),** 288, 1375-1384.

11) Misra T K and Sinha C. *Transition Metal Chemistry.* **(1999),** 24, 467-473.

12) Abdul Hussein H A. Thesis, M.Sc., University of Kerbala. **(2010)**

13) Lien M H and Hopkinson A C. *Journal of Physical Chemistry.* **(1984),** 88, 1513-1525.