

# Preparation and Study of Charge- Transfer Complexes for Acetylenic Amine Derivatives

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## ABSTRACT

Acetylenic amine derived from secondary amines such as piperidine , pyrrolidine and diethyl amine were synthesized as charge transfer donor have been treated with receptor I<sub>2</sub>, Br<sub>2</sub> and DDQ (DDQ = 2,3-Dichloro-5,6-Dicyano-p-Benzoquinone) to prepare transitional charge complexes . Benesi-Heldbrand equation have been used at ( $\lambda_{max}$ )for formation complexes to calculate potential ionize. Calculation for acetylenic amines derivatives at the first time from transitional energy with studied receptor and calculated equilibrium constant.

## Introduction:

Acetylenic amines are very important class of compounds for their pharmacological properties such as activity, low toxicity and easy to absorption from the body. Moreover these compounds are electron rich and easy to bond with receptor protein(1) . some of their pharmaceutical uses as anticancer (2) and hypotensives agent(3).

In investigating the importance of acetylenic bond for pharmacological activity it was though possible that the electron rich acetylenic bond attaches itself to the positive binding site in the cholinergic receptor, in which case its presence is probably necessary for the effect. It is also possible that the rigidity of the system serves the purpose of keeping the two nitrogen atoms at suitable distance from each other(4).

In this work acetylenic amines were used as donors in preparation of serious new complexes with various acceptor. This study is un presented and complexes between acetylenic amines and acceptor are not found in the literature.

## Materials & Methods:

### 1- INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to recorded the ir spectra as KBr, UV/VIS spectra were measured by a

HITACHI U-2000 spectrophotometer, Elemental Analysis (C.H.N) founded on (Carlo Erloa microanalyzer type 1106), Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

### 2-MATERIALS:

All material were supplied by BDHchemicals , the solvents , Ethanol Absolute ,diethylether and DMSO were supplied by Aldrich .

A- Preparation of the ligand:

Preparation of N,N-diethyl Propargyl Amine, N-Propargyl Pyrrolidine and N-Propargyl-3-methyl Piperidine were prepared according to the literature (5) .The full name of the acetylenic amines will be replaced by a number (L1,L2, L3) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L1, L2, L3) are listed in table (1). The characters ir bands and uv/vis spectrum in DMSO as shown in table (2), (3).

## RESULT AND DISCUSSION

Acetylenic Amines were used as donors in preparation of a serious new complexes with various acceptor . this study is un presented and complexes between acetylenic amine and acceptor are not found in the literature.(6)

Spectral measurements have been made to study charge transfer complexes formed from compounds interference (L1,L2, L3) with Iodine, Bromine and DDQ as acceptors in chloroform at room temperature in the Uv-Vis. region. The first step

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included finding high absorbance peak for complex formation between receptor concentration was hold constant ,but the donor concentration changed.

Charge transfer complexes between donors and the receptor DDQ:

The spectra results are listed in table (2) for the complexes of the receptor DDQ with compounds (L1,L2, L3). Formation equilibrium constant for donor complexes was high value, and this is clear because there is triple bond, which increases the ability to donate electron, moreover, the ionization potential (IP) for ligands (L1,L2, L3) can be calculated from transition energy for charge transfer complex  $h\nu$  and DDQ constants  $a=0.7$  ev,  $b=-3.86$  ev (7) as shown in the following formula  $h\nu=aIP+b$  in since the molecular structure for the prepared compounds is very similar the ionizing power values are equal or nearly equal.

Charge transfer complexes between donors and Iodine receptor :

Table (2,3) shows the spectral results and physical parameters for iodine complexes with donors by application Benesi-Heldbrand equation for the prepared complexes.

It is clear from equilibrium constant for complex formation that the charge transfer complexes with iodine are stronger than compared with its complexes with receptor DDQ, the reason for this belonged to the type of electron transfer, charge transfer complexes with Iodine is  $\pi-\alpha^*$ ,  $n-\alpha^*$  and with DDQ is  $\pi-\pi^*$ ,  $n-\pi^*$ , because the compounds contain nitrogen atom with (n) donor electrons and to CEC which gave  $\pi$  electrons and empty  $\pi$  orbital for group C=O of DDQ molecule. The ionizing power for the compounds can be calculated by the same way which was used with DDQ complex. The Iodine receptor constants were  $a=0.87$  ev,  $b=-3.6$  ev(8) table (3) show the IP for compounds (L1,L2, L3) which is calculated for charge transfer complexes with Iodine in ethanol solvent.

The ionizing potential power for each compound is found in table (3) was calculated in charge transfer complexes with Iodine and agree with calculated values in charge transfer complexes with DDQ in table (3) so that ionizable power mean for each compound in charge transfer with Iodine and DDQ receptor.

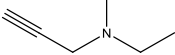
### Charge transfer complexes with Bromine as receptor :

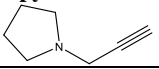
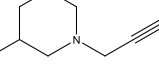
These complexes have been prepared by the same way which was followed to prepare charge transfer complexes with Iodine and DDQ, but it noticed that addition of bromine to the any compound solution, that the bromine color disappeared, then yellow precipitant which appears is indicative of the bromine ability to attack triple bonds, means there is chemical reaction between bromine and compounds (L1,L2, L3) charge transfer complexes cannot be detected.

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Table(1): physical properties of the ligands (L1,L2, L3).

No .	Name and structure of compound	Yield %	colour	M.P °C picrate	Elemental analysis % found (% cal.)			Ir spectra $cm^{-1}$	Uv-Vis. nm
					C	H	N		
L <sub>1</sub>	N,N-diethylprop-2-yn-1-amine 	82	Pale yellow	109-111	40.70 (40.68)	3.70 (3.66)	17.28 (17.25)	$\nu(\text{ECH})3300$ , $\nu(\text{CECH})2100$ , $\nu(\text{CH})2950$	311,382 In DMSO

L <sub>2</sub>	1-(prop-2-ynyl)pyrrolidine 	70	Pale yellow	145-146	46.65 (46.75)	4.44 (4.52)	15.56 (16.21)	$\nu(\text{ECH})3300$ , $\nu(\text{CECH})210$ 0, $\nu$ (CH)2968	308,389 In DMSO
L <sub>3</sub>	3-methyl-1-(prop-2-ynyl)piperidine 	90	Pale yellow	119-122	47.72 (47.69)	4.5 (4.45)	15.9 (15.87)	$\nu(\text{ECH})3310$ , $\nu(\text{CECH})211$ 0, $\nu$ (CH)2960	314,386 In DMSO

Table(2): Spectrophotometer results for Charge-Transfer complexes of ligands (L<sub>1</sub>,L<sub>2</sub>, L<sub>3</sub>) with (I and DDQ) at (298k)

[A°] *10 <sup>-4</sup>	Molar Ratio	Abs. L <sub>1</sub> DDQ	Abs. L <sub>2</sub> DDQ	Abs. L <sub>3</sub> DDQ	Abs. L <sub>1</sub> I	Abs. L <sub>2</sub> I	Abs. L <sub>3</sub> I
5	1:1	0.340	0.357	0.322	0.281	0.318	0.259
10	1:1	0.421	0.370	0.333	0.357	0.394	0.435
20	1:1	0.507	0.531	0.496	0.411	0.545	0.582
30	1:1	0.551	0.622	0.585	0.452	0.583	0.627
40	1:1	0.645	0.714	0.676	0.498	0.533	0.675
$\lambda$ max (nm)		522	535	540	411	423	435

Table(3): physical parameters for Charge transfer Complexes.

No.	$\lambda$ max	h $\nu$ /ev	I <sub>p</sub> /ev	K*10 <sup>-2</sup>	$\epsilon$ m <sup>2</sup> /Mol.	- $\Delta$ Gkg
L <sub>1</sub> DDQ	522	2.374	8.905	28.442	0.5783	8.292
L <sub>2</sub> DDQ	535	2.316	8.822	18.480	0.6920	7.224
L <sub>3</sub> DDQ	540	2.295	8.792	15.907	0.6720	6.853
L <sub>1</sub> I	411	3.015	7.603	23.278	0.5181	7.796
L <sub>2</sub> I	423	2.930	7.505	20.697	0.6191	7.505
L <sub>3</sub> I	435	2.849	7.412	8.171	0.9099	5.202

## تحضير ودراسة معقدات انتقال الشحنة لمشتقات الأمينات الاستلينية .

عمر حمد شهاب

الخلاصة:

تضمن البحث تحضير الأمينات الاستلينية المشتقة من الأمينات الثانوية كالبيبردين والبايرونولين وثنائي الاثيل أمين كمانحات ناقلة للشحنة وذلك بمعاملتها مع مستقبليات مختلفة I<sub>2</sub>,Br<sub>2</sub> و DDQ (DDQ = 2,3-Dichloro-5,6-Dicyano-p-Benzoquinone) لتحضير معقدات الشحنة الانتقالية. تم استخدام معادلة بنسي- هيلدبراند عند القيمة العظمى للامتصاصية ( $\lambda$ max) للمعقدات المتكونة لحساب جهد التاين. تم عمل الحسابات الخاصة بمشتقات الامينات الاستلينية والمحضرة لاول مرة كطاقة الانتقال مع المستقبليات اضافة الى حساب ثابت التكوين للمعقدات المتكونة.