Spectral and Thermodynamic Studies of Charge Transfer Complexes Derived From Schiff Bases with Some Electron Acceptors

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Abstract

(27) Schiff bases prepared product of by aldehyde and substituent aromatic (4-Methoxy,4-Bromo,4-Nitro,4,4Dimethylamine,4-Toulo) aldehyde with aniline and substituent aromatic (4-Bromo,4-Nitro,4-Methoxy,4-Amino) aniline , as charge donor with two acceptor (di nitro benzene, picric acid) . The Benesi - Hildebrand equation was used the effect of calculation equilibrium constant different polar solvent (CCl_4,CH_3OH,CH_2Cl_2,DMF). Ata temperature of (10-35)C^0 on eqilibrium and this is used to calculated it ,where the values negative were observe in the studied it Thermodynamic faction , The negative values of the enthalpy and Free energy Gibbs proved that, the formation of CTC is exothermic and could occur spontaneously .As Compare experimental result with theoretical were by uses program (ChemBio3D Ultra 11.0) .

Key Words : Schiff's bases ;Charge transfer complexes ;Temperature effect ; Computational Chemistry

دراسة طيفية وثرموديناميكية لمعقدات انتقال الشحنة المشتقة من قواعد شيف مع بعض المستقبلات الألكترونية

أ.د عبد الرحمن خضير الطائي دعاء اياد ياس البياتي
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الخلاصة

تم تحضير (27) من قواعد شيف الناتجة من تفاعل الالديهايد ومعوضاته (4-ميثوكسي ،4-برومو،4-نايترو4,4- ثنائي مثيل امين ،4-تولو) الديهايد مع الانيلين ومعوضاته (4-برومو،4-امينو،4-ميثوكسي ،4-نايترو)أنيلين كواهبات للشحنة مع المستقبلين (2-4-ثنائي نايتروبنزين ،1-3-5-ثلاثي نايترو فينول) وقد أستعملت معادلة بنسي –هلدبراند وذلك لحساب ثابت الاتزان لهذة المعقدات في مذيبات مختلفة القطبية (رباعي كلوريد الكاربون ،ثنائي كلوريد المثلين ،ثنائي مثيل فورممايد،الميثانول) من خلال تأثير درجة الحرارة على ثابت الاتزان عند المدى م^0 (35-10) وأستخدامها في حساب الدوال الثرموديناميكية ، وأن القيم للمعقدات التي حضرت والموضحة في هذة الدراسة تشير الى أن تكوين المعقد باعث للحرارة وتلقائي. وتم مقارنة النتائج العملية بالنتائج النظرية بأستخدام برنامج ChemBio3D Ultra). 11.0)

الكلمات المفتاحية : قواعد شيف ،معقدات انتقال الشحنة ، تأثير درجة الحرارة ، الكيمياء الحسابية

Introduction:

Schiff bases is organic compound continue azo methane group (-CH=N-)[1] . The study of the charge transfer complexes between several Schiff bases as electron donor and electron acceptor[2] , such as dinitrobenzene (DNB), picric acid (TNP) and aromatic nitro compounds have been investigated by many authors[3-7] ,The equilibrium constants , the extinction coefficients of the CT complexes and the ionization potential of the acceptors were calculated . The effect of the type of the substituent[8-11] on the ring of PhN and PhC of the Schiff bases were studies by using the IR , UV-visible ,and charge transfer complexes (CTC) with some acceptors exhibited wide applications[11]. Accordingly ,much interest have been paid to molecular CTC . The formation of molecular complexes of (CT) type played an important role in many biological processes[12]. In another study , new molecular complexes of the CT type derived from the reaction of Schiff bases derivative as a donor molecules with neutral molecules and acidic molecules as acceptors were synthesized [13] . In this work , the physical parameters of a number the CT complexes of (27) Schiff bases derived from aldehyde substituent and number of substituent aromatic amines as electron donors with two electron acceptors in different solvent[14] polarity (CCl_4,CH_3OH ,DMF,CH_2Cl_2) were calculated from their electronic spectra.

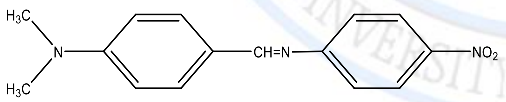
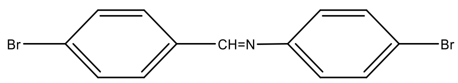
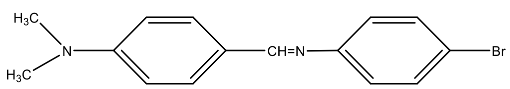
Experimental

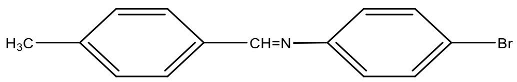
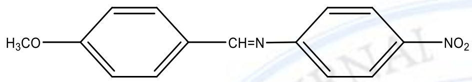
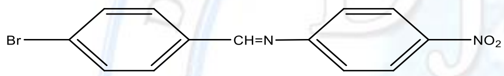
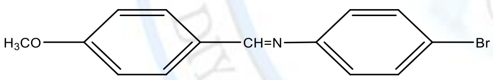
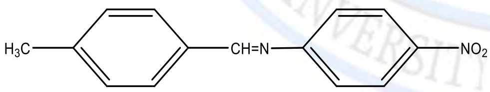
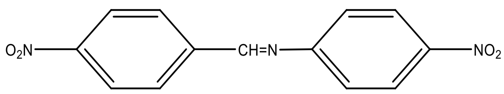
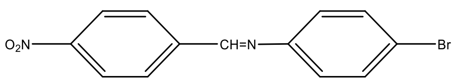
Reactive chemicals and solvents were supply from Merck, Aldrich Chemical Co. The compounds under study were structurally characterized from their ; Melting points (recorded with Electro thermal Melting point Apparatus), FT-IR spectra (recorded by FT-IR Spectrophotometer 8400 Schimadzu (KBr disc) and UV-Visible spectra (with recorded in ethanol as a solvent by Schimadzu -1650 pc spectrophotometer (a quartz cell of 1.0 cm path length).

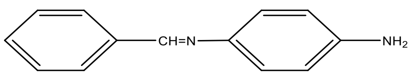
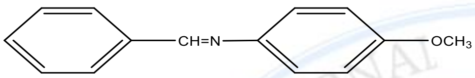
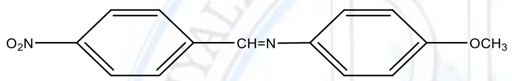
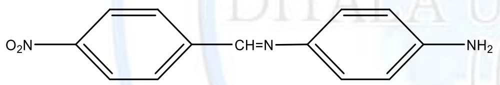
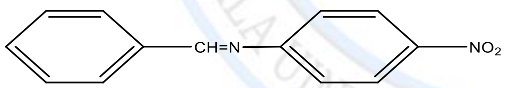
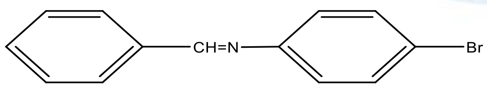
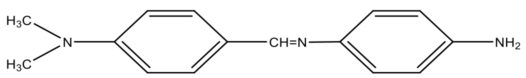
preparation of Schiff bases

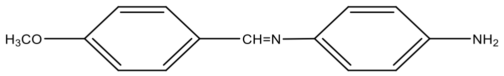
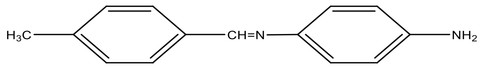
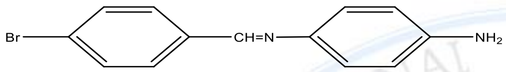
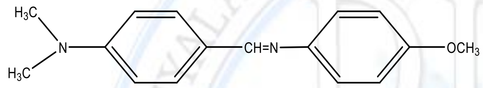
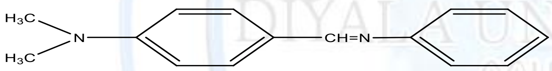
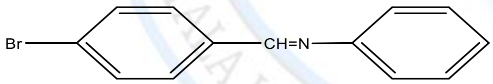
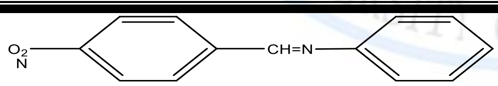
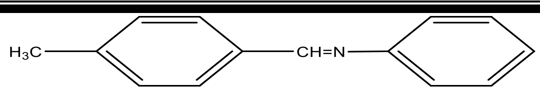
(27) Schiff bases were synthesized from the condensation of benzaldehyde and substituent aromatic with aniline and substituent aromatic in absolute ethanol following a similar procedure as in literature[1]. ; and the corresponding amine were refluxed for (2-6 hour) at (50C^{o}) in boiling point solvent and (10-15 ml) absolute ethanol . Upon cooling a crystalline product was separated,. The solid was recrystallized from ethanol or cyclohexane. The molecular structure of these Schiff bases were characterized by Spectrophotometer Fourier Transform infrared (FTIR) as KBr disc .

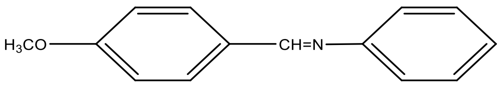
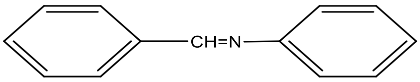
Table (1) : The melting point, and physical properties of prepared Schiff bases .

Com p.NO	الاسم العلمي والصيغة الكيميائية	M .wt (gm/ mole)	M.P ^{0}C	Color
1	 4-N,Ndimathylbenzyldene-4-Nitroaniline	269	115-118	Dark Green
2	 4-Bromobenzyldene- 4- Bromoaniline	338.8	140-143	White
3				

	4-N,Ndimathylbenzyldene-4-Bromoaniline	**302.9**	**155-158**	**Yellow**
4	 4-Tolubenzyldene-4-Bromoaniline	**273.9**	**124-126**	**White**
5	 4-Methoxybenzyldene-4-Nitroaniline	**256**	**107-110**	**Green**
6	 4-Bromobenzyldene-4-Nitroaniline	**304.9**	**169- 172**	**yellow**
7	 4-Bromoaniline4-4-Methoxybenzyldene	**289.9**	**100-103**	**White**
8	 4-Tolubenzyldene-4-Nitroaniline	**240**	**128-130**	**Dark green**
9	 4-Nitroaniline -Nitrobenzylden4-	**271**	**112-114**	**Dark yellow**
10		**304.9**	**160-163**	**Yellow**

	4-Nitrobenzyldene 4-Bromoaniline			
11	 Benzyldene-4-Aminoaniline	**196**	**104-106**	**White**
12	 Benzyldene-4-Methoxyaniline	**224**	**43-46**	**White**
13	 4-Nitrobenzyldene-4-Methoxyaniline	**269**	**120-123**	**Yellow**
14	 4-Nitrobenzyldene-4-Aminoaniline	**241**	**100-102**	**Yellow**
15	 Benzyldene-4-Nitroaniline	**226**	**100-102**	**Orang**
16	 Benzyldene-4-Bromoaniline	**259.9**	**57-60**	**White**
17	 4-N,Ndimathylbenzyaldene-4-Aminoaniline	**239**	**48-50**	**Orang**

18	 4-Methoxybenzyldene-4-Aminoaniline	**226**	**110-112**	**Light yellow**
19	 4-Tolubenzyldene-4- Aminoaniline	**210**	**108-110**	**Yellow**
20	 4-Bromobenzyldene-4-Aminoaniline	**274.9**	**130-133**	**White**
21	 4-N,Ndimathylbenzyldene-4-Methoxyaniline	**267**	**124-126**	**Yellow**
22	 4-N,Ndimathylbenzyldeneaniline	**224**	**93-96**	**Dark yellow**
23	 4-Bromobenzyldeneaniline	**259.9**	**80-83**	**White**
24	 4-Nitrobenzyldeneaniline	**239**	**87-89**	**yellow**
25	 4-Tolubenzyldeneaniline	**195**	**68-70**	**Light yellow**

26	 4-Methoxybenzyldeneaniline	**211**	**44-47**	**White**
27	 Benzyldeneaniline	**181**	**55-57**	**Light yellow**

Result And Discussion

1- Interpretation of IR Spectra

The major absorption bands of the IR spectra of the studied Schiff bases measured by using Shimadzu Spectrophotometer(FTIR) Fourier Transform with KBr disc , the important variation in the stretching vibrations of certain bands were as follows :

The bands appeared at (1640-1600)cm^{-1} are related to the stretching mode of the C=N bond, and disappear carbonyl group (C=O). the positions of the band are varied with changing the nature of the substituent's (x) on the ring PhN. The band shift generally to the higher wave numbers with increased acceptor character of the substituent (x) . The order of para substitution is in accordance with decreased polarization influence of the C=N group on the (x) substituent.

2. UV-Visible. The CT complexes solution have been investigated with acceptors using different solvent spectrometric ally at λ_{max} .The measurement of the optical densities of complexes at their λ_{max} were carried out after (30-60) minut from the preparation of complexes[6,15 ,16] . The used concentration of all acceptors ($1x10^{-4}$ M) was kept constant , and was much greater than the initial concentration of the acceptors (at least 10 times) in every

solution .This was done since the Benesi – Hildebrand's equation is applied under condition that held the CTC at (1:1) ratio of complexes .

The solution of all complexes in different solvent are obeyed Benesi-Hildbrand equation[17]

Equation (1) was used to calculate the extinction coefficients and equilibrium constants for our CT complexes[18] .

$$\frac{[A_o]}{A_{com}} = \frac{1}{\varepsilon_{AD}} + \frac{1}{K.\varepsilon_{AD}} \bullet \frac{1}{[D_o]} \quad \text{.................(1)}$$

$[A_0]$: Acceptor concentration

$[D_0]$: Donor concentration

$[A_{com}]$: Complexes Absorption

$[K.\varepsilon_{AD}]$: equilibrium constant to the complexes

$[\varepsilon_{AD}]$: coefficient molarity to the complexes

Table (2) : The K_{CT} (M^{-1}) and R^2 of their CTC (27) with acceptor (DNB) at 283 K in different solvent.

S.B	CCl_4		$ClCH_2Cl$		CH_3OH		DMF	
	K_{CT}	R^2	K_{CT}	R^2	K_{CT}	R^2	K_{CT}	R_2
1	2571	0.994	690	0.990	484	0.998	78	0.997
2	3400	0.994	998	0.998	510	0.990	52	0.993
3	3188	0.997	550	0.997	98	0.998	84	0.998
4	3400	0.998	1125	0.997	556	0.995	9	0.993
5	1200	0.997	1084	0.995	350	0.994	85	0.993
6	5000	0.995	740	0.998	420	0.995	28	0.998
7	2428	0.992	300	0.997	200	0.997	38	0.994
8	756	0.994	575	0.988	292	0.992	85	0.998
9	4666	0.998	325	0.997	285	0.995	12	0.998

10	3333	0.995	337	0.994	225	0.997	43	0.998
11	5633	0.995	970	0.991	670	0.986	200	0.999
12	5300	0.998	728	0.984	364	0.998	95	0.989
13	5633	0.995	623	0.995	483	0.996	31	0.997
14	5300	0.997	1100	0.998	640	0.996	112	0.995
15	1850	0.994	1058	0.997	607	0.995	51	0.998
16	3500	0.994	1095	0.998	342	0.993	23	0.998
17	5450	0.999	1304	0.998	211	0.992	33	0.999
18	1610	0.998	497	0.992	200	0.998	50	0.998
19	2084	0.997	636	0.996	633	0.982	200	0.995
20	1500	0.993	845	0.995	550	0.984	232	0.992
21	683	0.995	500	0.992	119	0.991	57	0.998
22	3680	0.993	582	0.992	446	0.999	57	0.999
23	3000	0.993	1048	0.999	275	0.995	94	0.993
24	4000	0.997	325	0.997	105	0.988	40	0.999
25	2600	0.994	414	0.989	300	0.992	58	0.998
26	1555	0.996	870	0.994	575	0.997	60	0.999
27	2714	0.999	255	0.994	53	0.996	33	0.996

Table (3) : The K_{CT} (M^{-1}) and R^2 of their CTC (27) with acceptor (TNP) at 283K in different solvent

S.B	CCl_4		$ClCH_2Cl$		CH_3OH		DMF	
	K_{CT}	R^2	K_{CT}	R^2	K_{CT}	R^2	K_{CT}	R^2
1	933	0.993	557	0.994	380	0.994	14	0.995
2	1333	0.998	923	0.995	257	0.994	61	0.997
3	1300	0.985	392	0.992	78	0.998	30	0.986
4	1828	0.997	583	0.997	507	0.994	90	0.987
5	650	0.993	650	0.993	250	0.993	47	0.998
6	1170	0.994	680	0.995	321	0.993	16	0.985
7	588	0.991	275	0.997	130	0.994	35	0.998
8	1010	0.980	350	0.994	177	0.995	75	0.996
9	623	0.995	915	0.997	140	0.999	13	0.997
10	430	0.994	450	0.988	81	0.995	30	0.996
11	983	0.991	483	0.988	384	0.998	100	0.987
12	1391	0.999	781	0.994	330	0.994	30	0.986
13	1216	0.998	692	0.996	433	0.995	100	0.984
14	5300	0.997	1100	0.998	640	0.996	107	0.993
15	1850	0.994	1058	0.997	607	0.995	54	0.992
16	3500	0.994	1095	0.998	342	0.993	82	0.980
17	5450	0.999	1304	0.998	211	0.992	46	0.992
18	1610	0.998	497	0.992	200	0.998	20	0.992

19	2084	0.997	636	0.996	633	0.982	250	0.992
20	1500	0.993	845	0.995	550	0.984	133	0.992
21	683	0.995	500	0.992	119	0.991	11	0.995
22	3680	0.993	582	0.992	446	0.999	34	0.998
23	3000	0.993	1048	0.999	275	0.995	68	0.999
24	4000	0.997	325	0.997	105	0.988	16	0.999
25	2600	0.994	414	0.989	300	0.992	160	0.982
26	1555	0.996	870	0.994	575	0.997	10	0.980
27	2714	0.999	255	0.994	53	0.996	15	0.999

In the other part of this work, the effect of temperature on the values of equilibrium constants K_{CT} in solvent (CCl_4) (283 - 308) K^0 for charge – transfer complex formation is investigated the value of ΔH, ΔG^0 and ΔS^0 for the CT complexes were calculated from the dependence of K_{CT} upon the temperature as in (Table 3) . The values proved that the formation of CTC are exothermic and spontaneous. The $\Delta G°$, $\Delta H°$, and $\Delta S°$ were calculated[16] using the equations :

$\Delta G° = -RT \ln K_{CT}$ ……………. (2)

$\ln K_{CT} = \Delta S°/R - \Delta H°/RT$ …………….. (3)

A plot of ln K_{CT} vs $1/T$ was found to be linear as show in fig (1) , ΔH and $\Delta S°$ determined from the slope and intercept respectively or : : $\Delta S° = (\Delta H - \Delta G°) /T$ …….(4)

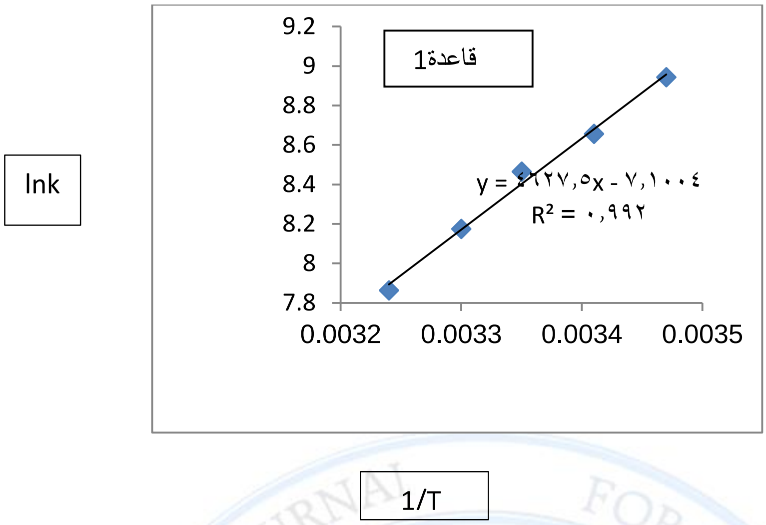


Fig (1) : A typical example of application A plot of ln K_{CT} vs 1/*T* the CT complex (1) with DNB acceptors in CCl_4 .

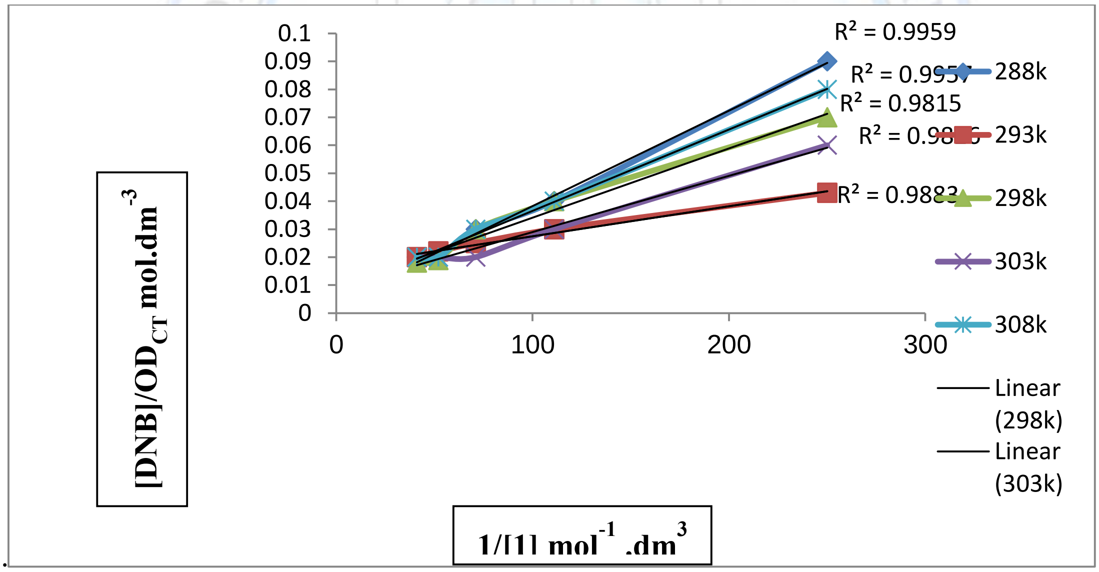


Fig (2) : A typical example of application of Benesi-Hildbrand equation for the CT complex (1) with DNB acceptors at different temperature in CCl_4

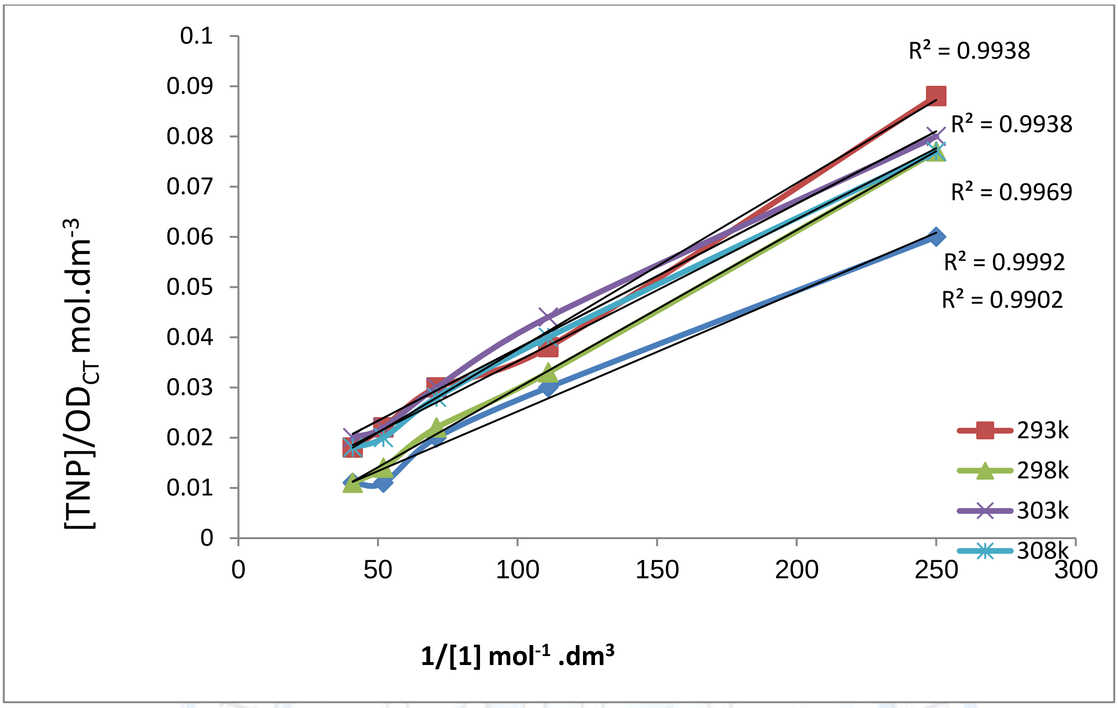


Fig (3) : A typical example of application of Benesi-Hildbrand equation for the CT complex (1) with TNP acceptors at different temperature in CCl_4 solvent .

Table (4) :Thermodynamic parameters of CTC (1-27) at various temperature in CCl_4 with two acceptors (ΔG^0 , ΔH in KJ.mol^{-1} and ΔS^0 KJ.mol^{-1}.k^{-1}) .

CTC.No	DNB			TNP		
	$-\Delta\bar{G}^o$	$-\Delta\bar{S}^o$	ΔH	$-\Delta\bar{G}^o$	$-\Delta\bar{S}^o$	ΔH
1	17.864	-148	-62.7	16.24	259	62.7
2	16.772	268.4	63.4	14.052	170.2	-64.7
3	17.276	262.8	61.2	16.902	56.86	61.3
4	17.574	244.4	55.4	12.544	-161.4	-60.7
5	16.508	272.6	64.9	17.592	-168.8	-68
6	15.006	278.6	68.1	23.042	-123.6	-60

7	18.094	-123.6	-55.1	13.541	93.8	14.7
8	14.882	-135	-55.3	16.11	134.4	24.11
9	15.708	237	55.1	17.252	-25.6	-25
10	15.982	219.2	49.5	17.796	-20.2	-23.9
11	14.542	215.2	49.7	16.936	-30	-26
12	18.152	248.2	55.9	15.884	156.6	30.4
13	16.416	76.2	-39.3	15.194	-171.6	-65.8
14	15.13	77.6	-38.4	12.544	-161.4	-60.7
15	16.016	62.4	-34.7	23.042	-158.4	-60
16	13.916	159.2	33.7	17.592	-168.8	-68
17	15.884	154.6	30.4	17.598	248.8	60
18	16.578	200.8	43.4	15.608	273.4	66
19	17.638	-80.6	-41.8	15.666	-94.6	-44
20	14.828	206.8	46.9	16.416	-76.2	-39.3
21	15.666	94.6	-44	15.52	196.2	43.1
22	15.666	-94.6	-44	16.976	-128.8	-55.5
23	18.464	23.04	50.3	16.344	-138.6	-57.7
24	15.372	239.6	56.1	15.004	-122.4	-51.6
25	16.976	128.8	-55.5	14.514	215.6	49.9
26	16.344	138.2	-57.7	14.23	80.4	51.6
27	15.004	122.4	-51.6	13.702	244.8	59.4

Finally , in theoretical study the physical parameters of the Schiff bases have been calculated quantum mechanism methods which is Semi- empirical (AM1).
by applying the program (ChemBio3D Ultra 11.0) .

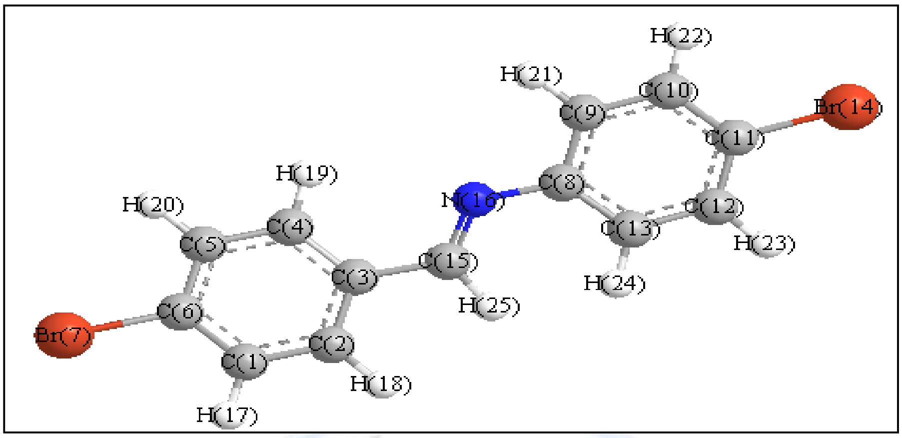


Fig (4) : A typical example of Schiff bases in a gas phase .

Table (5) : The various The physical parameters of Schiff bases(1) in different solvent

Solvent المذيب	DE ثابت العزل	K ثابت الاتزان	Δ(L-H) الفرق الطاقي	W(ev) دليل الالكتروفيلية الكروي	η(ev) الصلادة	μ (ev) الجهد الإلكتروني الكيميائي	Charge Ne شحنة موليكان
CH_3OH	*32.62*	484	0.2416	0.1535	0.1208	-0.1926	-0.1845
CH_2Cl_2	10.1	690	0.2412	0.1536	0.1206	-0.1925	-0.1905
CCl_4	2.24	2571	0.2404	0.1544	0.1202	-0.1927	-0.1941

Table (6) : The various physical parameters of CTC(1) with DNB in different solvent

Donor		Acceptor		
HOMO(e.v)	LUMO(e.v)	HOMO(e.v)	LUMO (e.v)	Δ(L-H)
-0.3128	-0.0726	-0.4273	-0.0994	0.2134
-0.3379	-0.0335	-0.4273	-0.0994	0.2385
-0.3010	-0.0182	-0.4273	-0.0994	0.2016
-0.3282	-0.0285	-0.4273	-0.0994	0.2288
-0.3420	-0.0766	-0.4273	-0.0994	0.2426

Table (7) : The various physical parameters of CTC(1) with TNP in different solvent

Donor		Acceptor		
HOMO(e.v)	LUMO (e.v)	HOMO (e.v)	LUMO(e.v)	Δ(L-H)
-0.3128	-0.0726	-0.4339	-0.1306	0.1822
-0.3379	-0.0335	-0.4339	-0.1306	0.2073
-0.3010	-0.0182	-0.4339	-0.1306	0.1704
-0.3282	-0.0285	-0.4339	-0.1306	0.1976
-0.3420	-0.0766	-0.4339	-0.1306	0.2114

In the theoretical study founded to the physical parameters of CTC with two electron acceptor (DNB,TNP) , for to the values interaction between donor and acceptor , on through values energy differencing Δ(L-H) was very few between HOMO and LUMO because happened inter molecular , So founded the values (W) effect group substituent on ($N(CH_3)_2$) , was few in some Schiff bases because increase interaction with solvent polar , So could the values stability constant of charge transfer complexes from to the reaction donor with accepter on solvent polarity was few we compare on non solvent polarity ,the values dielectric constant accepted with the values (K,W,ΔL, η) .

Conclusions

Each one of the compounds (1-27) under consideration , interact with acceptor molecules to form CT complexes . takes place through $n \rightarrow \pi^*, \pi \rightarrow \pi^*$ type transitions .The solutions of all complexes obeyed to Benesi -Hildebrand's equation . The ratio of Schiff bases derivative : acceptor in every cases is 1:1. the values of the physical parameters for compounds (1-27) and CT complexes (Ip , E_{CT} ,W, K_{CT} , ε_{CT} , ΔG°,ΔH ,ΔS°) were calculated , and found to be affected with both the nature of acceptors and the substituents on compounds (1-27) ,and for K_{CT} various decrease in solvent polarity compared with non polarity solvent . The CT complex were spontaneously ,but very weak in solution (negative value ΔH) with have a slower rate of the hydrolysis was observed . Finally inter molecular interaction between donor and acceptor were theoretical studied by program(ChemBio3D Ultra 11.0) .

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