

Thermodynamic Study of the Interaction of Benzylideneaniline with the Shift Reagent Cu (I) by U.V Spectroscopy

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Abstract

The U.V. spectra of series of benzylidene (mono and di- substituted) anilines have been studied with the shift reagent Cu (I). Addition of shift reagent causes a decrease in the absorption of A1 & A2 bands which may be attributed to the complex formation with Cu (I). The equilibrium constant for the process was calculated using the method of Hartman. The thermodynamic parameters ($\Delta G, \Delta H, \Delta S$) were obtained. Application of Skalski method show that the interaction with Cu(fod) is 1:1.

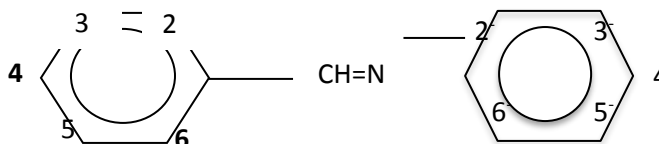
Keyword: Series of benzylidene, Cu(fod) UV spectroscopy, method of Hartman, Skalski method, absorption of A1 & A2.

1. Introduction

Benzylideneanilines are present mainly in the stable trans form [1]. The ¹H NMR and ¹³C NMR studies [2,3] of these compounds after addition of LSREu(fod)₃ show that they undergo isomerization to the less stable cis form.

The interaction of benzylideneaniline with LSR by U.V spectroscopy [4] and their thermodynamic behavior [5] have been studied. New binuclear shift reagent [6] have been used recently with cinnamylidene aniline [7].

The present work involves the study of the interaction of a series of benzylideneanilines (scheme 1) with another shift reagent Cu(I) (fod), which can interact with the olefinic and aromatic compounds.



1	4 = Cl	5.	4 = OCH ₃
2	4 = F	6.	4 = OCH ₃ , 4 = F
3	4 = OH	7.	4 = OCH ₃ , 4 = Br
4	4 = CH ₃	8.	4 = OCH ₃ , 4 = CH ₃

Scheme 1: Interaction of a series of benzylideneanilines

Note: Only the substituted position were mentioned

2. Experimental

Benzylidene anilines were prepared by mixing an equimolar amount of benzaldehyde and substituted benzaldehyde with aniline and substituted aniline according to the procedure described by El-bayoumi [8] and coworkers.

3. Preparation of the Shift Reagent Cu (I) (Fod) [9]

(1,1,1,2,2,3,3- heptafluoro- 7,7- dimethyl -4,6-octane dion) copper [1].

A solution of 9.6g (0.0324 mol) of pr(fod)₃ in (5 ml) of methanol was neutralized with 8.1 ml of (4 M) NaOH. The solution was added to a stirred solution of 5.5g (0.0324 mol) of copper nitrate in (75

ml) of distilled water. A precipitate immediately separated, was collected by suction filtration, and was dried under Vacuum.

4. Sampling

A stock solution of (5 x 10⁻³ M) Cu(I) (fod) was prepared in CCl₄, a solution of (5 x 10⁻⁴ M) of Schiff base was used for measurement. To (10 ml) of (5 x 10⁻⁴ M) solution of Schiff-base a different amount of (4 x 10⁻³ M) Cu was added using a micro syringe.

5. Measurements

The U.V. spectra were measured by Unicam Sp 800 U.V. spectrometer using (1 cm) silica cell. Measurements were performed against a blank solution containing only Cu (I) (fod) of

the same concentration as the sample in order to cancel the absorbance of the shift reagent.

Variable temperature measurements were performed between (293-343K⁰). Temperature control was carried out using a thermostat of a type HAAKED₃ (± 0.1 Temp.accuracy).

6. Results & Discussion

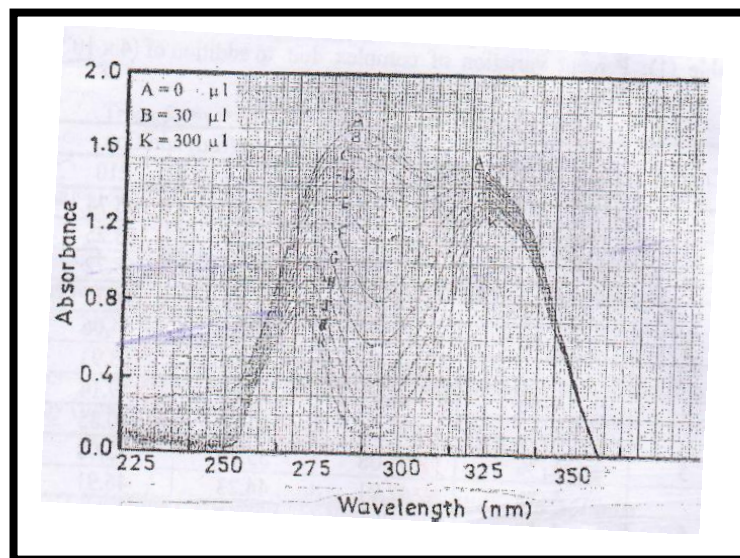


Fig. 1: absorption spectra of 4- methoxybenzylidene ,4- bromoanilin with Cu(I) in CCl₄

Successive additions (30 μ l) of Cu(I) up to (360 μ l) resulted in a decrease in the absorbance of (A_1 & A_2) but band A_1 undergoes more decrease than band A_2

A) in the absence of Cu(I) (fod)

B) in the presence of Cu(I) (fod)

The calculated values of (A_1 %) and (A_2 %) (Table 1) show a decrease in (A_1 %) and increase in (A_2 %) which may be due to complex formation of trans form with Cu(I) followed by transformation to the complex of the less stable cis form.

The U.V spectra of benzylideneanilines in CCl₄ (5×10^{-4} M) show a strong absorption band and a shoulder band, addition of the shift reagent Cu(I) (4×10^{-3} M) to benzylidene anilines causes a decrease in the both absorption bands (A_1 & A_2), band A_1 shifted to shorter wavelength (blue shift), while band A_2 to the longer wavelength (Fig 1).

In order to calculate the thermodynamic parameters variable temperature measurements were performed for solutions of benzylidene anilines (5×10^{-4} M) in CCl₄ with (210 μ l) of (4×10^{-3} M) Cu(I) (fod).

The equilibrium constant was calculated using the method of Hartmanin [9] which the equilibrium constant is correlated with absorptions of the two bands (A_1 & A_2) as follows:

$$K = \frac{A_2 a_1}{A_1 a_2}$$

Table 1: percent variation of complex due addition of (4×10^{-3} M) Cu(I) (fod) to benzylidene aniline (5×10^{-4} M) in CCl₄

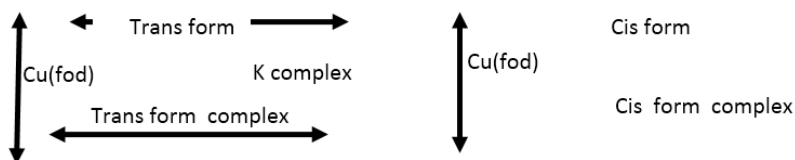
Comp	A1 % & A2%	Cu (fod) addition			
		30	90	210	300
1	A1 %	54.24	52.71	45.74	43.50
	A2 %	47.75	49.28	52.25	59.49
2	A1 %	64.00	66.16	66.72	66.02
	A2 %	36.00	35.83	35.27	35.97
3	A1 %	50.52	50.51	44.06	38.49
	A2 %	49.47	51.48	54.93	60.50
4	A1 %	61.93	61.29	58.14	57.86
	A2 %	38.06	38.70	41.85	43.13
5	A1 %	58.08	55.76	53.08	48.80
	A2 %	43.91	44.23	46.91	51.19
6	A1 %	56.70	54.28	50.66	45.35
	A2 %	45.29	45.71	49.33	54.64
7	A1 %	53.39	50.34	43.10	36.54
	A2 %	48.60	49.65	56.89	63.45
8	A1 %	56.96	53.95	47.39	42.05
	A2 %	45.59	46.04	52.60	57.94

Where a_1 & a_2 represent the molar absorption coefficients of band (1 & 2) after addition of Cu(I) (fod), A_1 & A_2 are the absorption of bands (1 & 2) respectively. Plot of A_2 vs A_1 at different temperatures gave straight lines with slopes $\frac{a_1}{a_2}$ from which the values of K has been calculated and given in (Table 2).

The following thermodynamic relation was used to calculate the enthalpy and entropy of the complex

$$\text{Log } K = \frac{-\Delta H}{2.303 RT} + \frac{\Delta S}{2.303 R}$$

Plot of $\log K$ against ($\frac{1}{T}$) give slopes of ($-\Delta H/2.303 R$) and an intercept ($\Delta S/2.303 R$). Such plot and the values of (ΔH & ΔS) are given in (Table 2). From these results it can be seen that equilibrium constant values decrease on increasing temperature, which is probably due to the decrease of stability of the cis form complex. The positive value of (ΔG) indicate that the equilibrium prefers the backwards transformation (cis complex back to trans see scheme (2)). The negative values of (ΔS) indicate that the complex is more ordered and more rigid



Scheme 2: Backwards transformation

In order to verify such proposed mechanism further work is needed using NMR spectroscopy (future work)

Stoichiometry (complex formation) of benzylidenaniline with Cu(I) (fod):

In addition to the decrease of absorbance of the two bands (A_1 & A_2) on adding Cu (I) (fod), a blue shift to shorter wavelength

and a red shift to the longer wavelength was also observed. The plot of frequency (Δy) [10] against the added amount of Cu (fod) for compound [7] show a linear correlation which have been obtained for both (A_1 & A_2) (Fig 2).

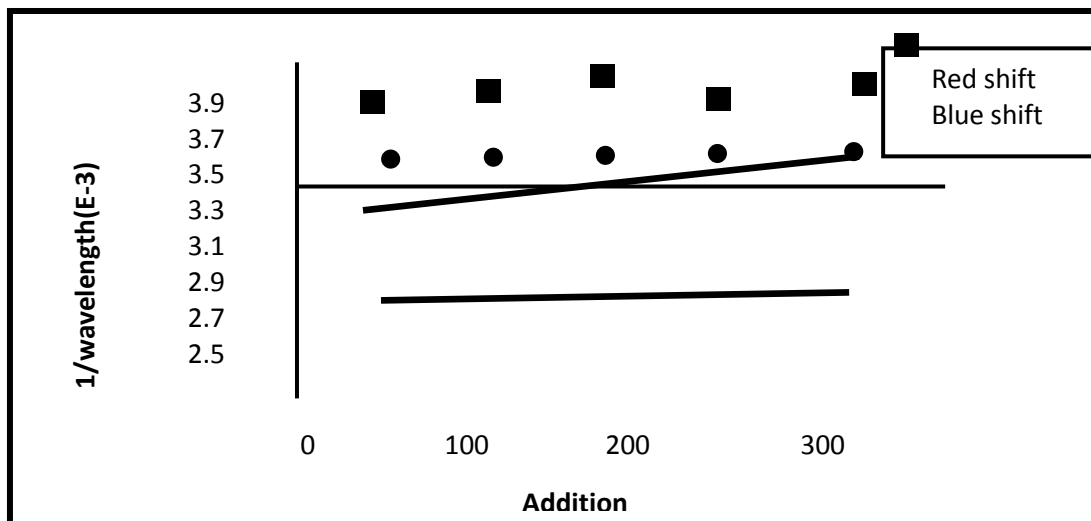


Fig. 2: Plot of frequency (Δy) against addition of Cu (I) (fod) for 4-methoxybenzylidene-4-bromo aniline for both bands (A_1 & A_2)

The slope of the plot was found to be (8×10^{-4}) for band A_1 (blue shift) and (2×10^{-4}) for band A_2 (red shift). This result indicates that the red shift (band A_2) is more affected with complexation with Cu (fod). In order to find the stoichiometry of these complexes a plot of $A_0 - A/[Cu(fod)]$ against A [where A_0 = the absorbance of the shift base at a particular wavelength in the absence of Cu (fod), A = the

absorbance in the presence of Cu (I) (fod)] was obtained with a linear correlation when $n=1$ (Fig 3) which represents the no. of Cu (fod) molecules involved in the complex.

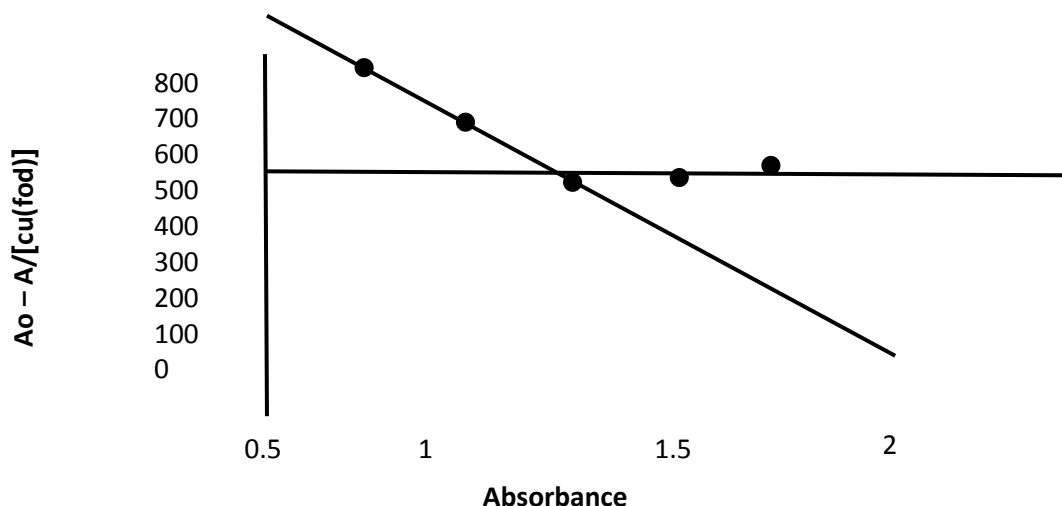


Fig. 3: plot of $A_0 - A/[Cu(I)(fod)]$ against absorbance for 4-methoxybenzylidene-4-bromo aniline

Table 2: The thermodynamic parameters of benzylidene anilines with Cu (I) (fod) at different temperature in CCL4

Comp.1

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	1.28	1.05	0.4827	0.7146	1619.90	-1470.04	-10.81
303	3.300	1.27	1.04	0.4759	0.7096	1713.02		-10.86
313	3.194	1.23	1.03	0.4670	0.7321	1821.66		-10.91

323	3.095	1.18	1.01	0.4644	0.7278	2007.18		-10.78
333	3.003	1.13	1.00	0.4526	0.7508	2213.15		-10.86

*average value of $\Delta S = -10.86$ **Comp.2**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	0.71	1.19	0.8521	0.0389	118.12	-219.08	-1.48
303	3.300	0.68	1.16	0.8342	0.0478	156.26		-1.050
313	3.194	0.66	1.13	0.8398	0.0430	145.32		-1.42
323	3.095	0.63	1.06	0.8382	0.0420	146.18		-1.40
333	3.003	0.61	1.02	0.8281	0.0520	161.76		-1.48

*average value of $\Delta S = -1.46$ **Comp.3**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	1.46	1.124	0.4080	0.5753	1545.04	-42.34	-7.13
303	3.300	1.44	1.120	0.4070	0.5745	1624.46		-6.16
313	3.194	1.43	1.114	0.4051	0.5762	1687.57		-6.14
323	3.095	1.42	1.110	0.3893	0.5863	1767.98		-6.18
333	3.003	1.41	1.100	0.3852	0.5945	1822.76		-6.12

*average value of $\Delta S = -6.16$ **Comp.4**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	0.89	1.28	0.7215	0.1855	475.01	-744.17	-3.45
303	3.300	0.85	1.24	0.741	0.1871	387.41		-3.34
313	3.194	0.81	1.28	0.7181	0.9018	426.74		-3.31
323	3.095	0.76	1.14	0.7022	0.2101	499.12		-3.46
333	3.003	0.71	1.08	0.6941	0.2191	543.82		-3.47

*average value of $\Delta S = -3.47$ **Comp.5**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	0.088	1.10	0.3998	0.6913	1822.10	-2248.37	-13.48
303	3.300	0.86	1.08	0.3236	0.7128	1927.20		-13.40
313	3.194	0.82	1.06	0.3712	0.7380	2001.65		-13.46
323	3.095	0.77	1.04	0.3621	0.7760	2177.65		-13.42
333	3.003	0.72	1.03	0.3531	0.7920	2269.28		-13.46

*average value of $\Delta S = -13.49$ **Comp.6**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	1.12	1.10	0.3066	0.7998	2092.03	-1908.11	-13.31
303	3.300	1.10	1.09	0.3020	0.8088	2187.11		-13.15
313	3.194	1.06	1.07	0.2966	0.8274	2341.83		-13.18
323	3.095	1.03	1.06	0.2870	0.8465	2512.83		-13.14
333	3.003	0.97	1.04	0.2613	0.8765	2673.25		-13.21

*average value of $\Delta S = -13.26$ **Comp.7**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	1.34	1.01	0.4908	0.4264	1182.09	-708.71	-6.13
303	3.300	1.31	1.00	0.4903	0.4280	1257.65		-6.14
313	3.194	1.29	0.99	0.4802	0.4331	1316.42		-6.10
323	3.095	1.26	0.98	0.4725	0.4466	1497.55		-6.13
333	3.003	1.23	0.96	0.4706	0.4501	1520.01		-6.08

*average value of $\Delta S = -6.12$ **Comp.8**

Temp. K^0	$\frac{1}{T} \times 10^3$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole.k
293	3.412	1.21	1.14	0.7440	0.1811	341.00	-621.89	-2.86
303	3.300	1.18	1.12	0.7170	0.1886	384.99		-2.85
313	3.194	1.16	1.10	0.7178	0.1876	398.10		-2.76
323	3.095	1.11	1.07	0.7041	0.2040	437.86		-2.83
333	3.003	1.06	1.03	0.7032	0.2120	449.86		-2.74

*average value of $\Delta S = -2.91$ **References**

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