

Study of Charge Transfer Complexes of salicylidene aliphatic amines with Eu(fod)₃ in cyclohexane by U. V. spectroscopy

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ABSTRACT

Salicylidene aliphatic amines in cyclohexane form 1:1 charge transfer complexes on addition of Eu(fod)₃, indicated by the observation of a new band in their U.V. spectra located at longer wavelength ($\lambda = 400$ nm) and with low extinction coefficient. The colorless solutions of Schiff-bases were changed to yellow on complexation with the shift reagent Eu(fod)₃.

Equilibrium Constant values (K) for the complexes were obtained by applying Benesi-Hildebrand equation. The factors which affected the values of K like the charge on N, O & C (ChN, ChO, ChC), steric energy, O-N distance, the dihedral angles (dh1 and dh2) were established computationally and were inserted into an equation of multiple linear regression as independent variables with K as dependent variable:

$$K = -1288.806 - 1653.722\text{ChN} - 40.197\text{ChO} - 914.560\text{ChC} + 507.207(\text{O-N dist.})$$

From the equation it is seen that the most effective factor is ChN which means that increasing ChN causes more availability of the lone pair of electrons on nitrogen which facilitate the interaction with Eu(fod)₃, and thus leading to higher K-value.

دراسة معقدات انتقال الشحنة للسالسدلين الامينات الالفاتية مع Eu(fod)₃ في الهكسان الحلقي بواسطة طيف الاشعة فوق البنفسجية

المخلص

تكون مركبات السالسدلين امين الالفاتية في مذيب السايكلو هكسان معقدات انتقال الشحنة من نوع 1:1 عند اضافة كاشف الازاحة Eu(fod)₃، ويستدل على ذلك من ظهور حزمة جديدة في اطراف الاشعة فوق البنفسجية عند طول موجي بحدود 400 nm وبمعامل انطفائية واطي. كما لوحظ ان المحاليل عديمة اللون لقواعد شيف قد تغيرت الى محاليل صفراء عند تكون هذه المعقدات.

وتم ايجاد قيم ثوابت الاتزان (K) لهذه المعقدات باستخدام معادلة بنسي هلدبراند، ومن ثم دراسة تأثير بعض العوامل على K مثل: الشحنة على الكاربون ، الاوكسجين، النتروجين (ChC, ChO, ChN)، طاقة الاعاقة، المسافة O-N والزوايا بين المستويين dh1 و dh2. وادخلت هذه العوامل في معادلة الاتحدار الخطي كمتغيرات مستقلة بينما اعتبرت K متغيرا غير مستقل:

$$K = -1288.806 - 1653.722\text{ChN} - 40.197\text{ChO} - 914.560\text{ChC} + 507.207(\text{O-N dist.})$$

من هذه المعادلة يتضح ان اكثر العوامل تأثيرا هو ChN وهذا يعني ان زيادة ChN تجعل زوج الالكترونات على النتروجين اكثر توفرا مما يسرع في عملية الاتحداد مع كاشف الازاحة $\text{Eu}(\text{fod})_3$ وبذلك تزداد قيم K.

INTRODUCTION

The effect of the lanthanide shift reagent $\text{Eu}(\text{fod})_3$ on the U.V spectra of benzylidene-anilines (Sulaiman *et al.*, 1993; Saleem and Al-Razzak, 1996) cinnamylidene-aniline (Sulaiman *et al.*, 1998; Saleem and Al-Razzak, 1997), benzylidene and cinnamylidene-aliphatic amines (Sulaiman *et al.*, 1997) and benzylideneamino-pyridine (Saleem *et al.*, 2001) compounds has been investigated. The effect results in a splitting of the absorption bands in the U. V spectra of the Schiff bases into two well defined bands. This was explained as being due to cis-trans isomerization of the Schiff base molecules. These observations have been supported by NMR studies (Saleem, 1982; Al-Rawi and Saleem, 1989; Saleem and Omar, 1994; Saleem and Al-Razzak, 2000).

The aim of the present work is to study the effect of $\text{Eu}(\text{fod})_3$ on the U. V spectra of a series of Salicylidene aliphatic amines in cyclohexane.

The compounds studied are listed below:

Salicylidene methyl amine	I
Salicylidene isopropyl amine	II
Salicylidene n-butyl amine	III
Salicylidene isobutyl amine	IV
Salicylidene allyl amine	V
Salicylidene cycloheptyl amine	VI

EXPERIMENTAL

Salicylidene-aliphatic amines were prepared (El-Bayoumi *et al.*, 1971) by mixing equimolar amounts of purified aliphatic amines and salicylaldehyde (it is preferable to add a slight excess of amine to ensure complete reaction of the aldehyde), a small amount of K_2CO_3 was added, then the mixture was allowed to stand over night. The oily condensation product was then extracted with anhydrous diethyl ether. Ether was evaporated and the residual oil was distilled and vacuum dried.

Instrumentation

The UV absorption spectra were recorded using Shimadzu UV-160 recording spectrophotometer, and SP 800 UV spectrophotometer (unicam) connected with Haake thermostat type 000-4526 for temperature regulation, using $1 \times 1 \times 3$ cm³ silica cells.

Measurements

A stock solution of 10^{-2} M of each Schiff base, and a stock solution of 10^{-2} M Eu(fod)₃ were prepared in (C.H.).

The UV spectra of Schiff bases show three absorption maxima in the range 232-234, 257-259, and 318-320 nm, these spectra were recorded for samples containing the optimum concentration of Schiff-base which is fixed experimentally.

To this solution successive additions (10,20,30,---, μl) of 10^{-2} M Eu(fod)₃ were performed.

Complex Formation :

To prepare the complex between S.B and Eu(fod)₃ in C.H, 500 μl of 10^{-2} M S.B was made 3ml total volume with C.H and successive additions of 10^{-2} M Eu(fod)₃ (10, 20, 30, 40 and 50 μl) to both sample and reference cells.

Determination of K Value:

K-values were estimated according to Benesi-Hildebrand (Benesi *et al.*, 1949) equation:

$$\frac{[A_o]}{A_{com}} = \frac{1}{\epsilon} + \frac{1}{K \cdot \epsilon} \cdot \frac{1}{[D_o]}$$

[D_o]: The molar concentration of Eu(fod)₃.

[A_o]: The molar concentration of S.B.

the plot of $\frac{[A_o]}{A_{com}}$ against $\frac{1}{[D_o]}$ result in a straight line, the intercept of the line = $(\frac{1}{\epsilon})$ from which ϵ (the molar extinction coefficient of the complex) was calculated. From the slope of the line $(\frac{1}{K \cdot \epsilon})$, the equilibrium constant K value of the complex was evaluated.

The Nature of Complex :

The nature of these complexes was determined by Job method. It was shown that the ratio of S.B to Eu(fod)₃ is 1:1.

Computation Calculations:

To perform the computational calculation for the Schiff bases under consideration, a package CS Chem. Office containing CS Chem. Draw ultra and CS Chem. 3D Pro was applied using a computer with a Pentium 4 processor inside.

The first step in this calculation is to select the program CS Chem. Draw Ultra, to draw the 2-dimensional structure of the molecule, name it, then paste the molecule into a new page of the program CS Chem. 3D Pro.

To draw the 3-dimensional structure of the compound showing the serial number of each element symbol, and save it in a selected titled directory.

MOPAC was applied to obtain some physical properties of the S.B including the electron densities and charges of the various atoms, bond length, bond angle, the atomic orbital electron populations, and the final heat of formation.

These data were calculated from the most stable configurations obtained by energy minimization procedures using AM1.

The steric energy was also calculated from these configurations using MM2.

RESULTS AND DISCUSSION

The U. V. absorption spectrum of $1.96 \times 10^{-4} \text{M}$ solution of salicylidene-*n*-butylamine (III) in C.H. show absorption maximum at 259 nm and two other bands at 234 nm and 320 nm. Successive additions of 10^{-2}M solution of $\text{Eu}(\text{fod})_3$ in C. H. to solution of salicylidene aliphatic amines caused a gradual decrease in the intensity of the observed bands of the whole S.B. spectrum, accompanied by a gradual appearance of a new long wavelength band at about 400 nm. The intensity of this band which is attributed to the complex formation between the Schiff base and the $\text{Eu}(\text{fod})_3$ increases, (Fig. 1).

The initial molar concentrations of the donors (Schiff base), the acceptor [$\text{Eu}(\text{fod})_3$] and the measured absorbance of the complex (A_{com}) for the salicylidene aliphatic amines (I to VI) with $\text{Eu}(\text{fod})_3$ in C. H are shown in Table (1).

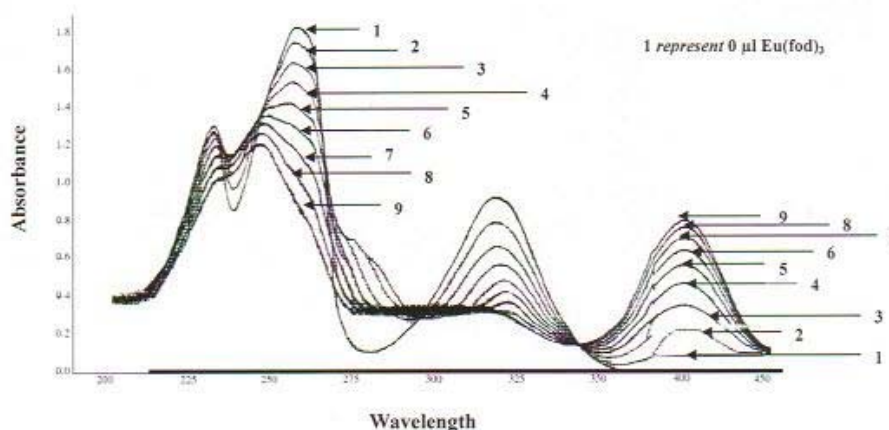


Fig. 1: The U.V spectra of $2 \times 10^{-4} \text{M}$ Salicylidene-*n*-butylamine in cyclohexane after successive addition of (10, 20, 30, ... μl) of 10^{-2}M $\text{Eu}(\text{fod})_3$.

Table 1: The measured absorbance of complexes of Salicylidene aliphatic amines (I to VI) on addition of different amounts of $\text{Eu}(\text{fod})_3$

[D ₀] Schiff bases	[A ₀] Eu(fod) ₃	A _{com.}					
		I	II	III	IV	V	VI
0.1661x10 ⁻²	0.332x10 ⁻⁴	0.21	0.31	0.31	0.30	0.31	0.19
0.1656x10 ⁻²	0.6623x10 ⁻⁴	0.34	0.54	0.54	0.54	0.55	0.23
0.1650x10 ⁻²	0.9901x10 ⁻⁴	0.46	0.75	0.78	0.75	0.77	0.30
0.1645x10 ⁻²	1.3158x10 ⁻⁴	0.56	0.95	0.98	0.95	0.98	0.35
0.1639x10 ⁻²	1.6393x10 ⁻⁴	0.66	1.14	1.18	1.15	1.18	0.39
Intercept*		-6.3865x10 ⁻³	-2.5377x10 ⁻³	-2.3822x10 ⁻³	-2.244x10 ⁻³	-2.1931x10 ⁻³	-0.017
Slope*		1.0886x10 ⁻⁵	4.4003x10 ⁻⁶	4.1362x10 ⁻⁶	3.9163x10 ⁻⁶	3.8266x10 ⁻⁶	2.8561x10 ⁻⁵
R*		0.9799	0.9730	0.9879	0.9739	0.9739	0.9705

* These values were obtained from the plot of $\frac{[A_0]}{A_{com}}$ against $\frac{1}{[D_0]}$ Where intercept = $(\frac{1}{\epsilon})$, slope = $(\frac{1}{K \cdot \epsilon})$, R = correlation coefficient.

K-values were calculated at 293K⁰ to Benesi-Hildebrand equation, their values are given together with the molar extinction coefficient values (ϵ) in Table (2).

Table 2 : The calculated /equilibrium constants, the molar extinction coefficient and λ_{max} values of complexes of Salicylidene aliphatic amines with $\text{Eu}(\text{fod})_3$ in C. H.

Complex	K (mole ⁻¹)	ϵ (lit.mole ⁻¹ .cm ⁻¹)	λ_{max} (nm)
I	587	157	400
II	576	394	400
III	577	419	402
IV	573	445	402
V	573	445	402
VI	595	59	400

From Table (2) it can be seen that the extinction coefficients values ($\epsilon < 1000$) together with the low intensity and long wavelength properties confirms that the transition is $n \rightarrow \pi^*$ and that the interaction between $\text{Eu}(\text{fod})_3$ and the Schiff base through the lone pair electrons of nitrogen or nitrogen and oxygen. It can be seen that K-values in the order: Salicylidene-cycloheptylamine > Salicylidene-methylamine > Salicylidene-n-butylamine > Salicylidene-isopropylamine > Salicylidene-isobutylamine = Salicylidene-allylamine.

The availability of electrons on the nitrogen atom and the tendency of $\text{Eu}(\text{fod})_3$ towards these electrons determine the K-value of the complex. Therefore the charge of nitrogen ChN and oxygen ChO was calculated for these Schiff bases by computation calculations, and plots were performed versus K-values of the complexes, non-linear relationship was obtained which indicates that other factors may affect the K-values of these complexes.

For this reason the steric energy (S), charge of carbon (ChC), the oxygen-nitrogen distance (O-N dist), dihedral angle (dhl) (11, 10, 9, 8), and dh2 (9,8,5,4) were calculated see Table (3) and Fig. (2).

Table 3: The calculated physical properties of the Schiff bases.

Compound	ChN	ChC	ChO	Steric energy (S) Kcal/mole	O-N dist. (Å)	dh1	dh2	K L.mol ⁻¹
I	-0.2366	-0.0060	-0.2586	4.777	2.90	121.5	0.0	587
II	-0.2327	-0.0030	-0.2592	7.257	2.89	110.3	1.3	576
III	-0.2340	-0.0024	-0.2587	7.245	2.89	114.3	1.4	577
IV	-0.1591	-0.0242	-0.2382	14.578	3.09	115.3	65.0	573
V	-0.1575	-0.0192	-0.2402	13.704	3.10	116.4	-66.7	573
VI	-0.1559	-0.0212	-0.2414	30.399	3.19	-119.4	-73.9	595

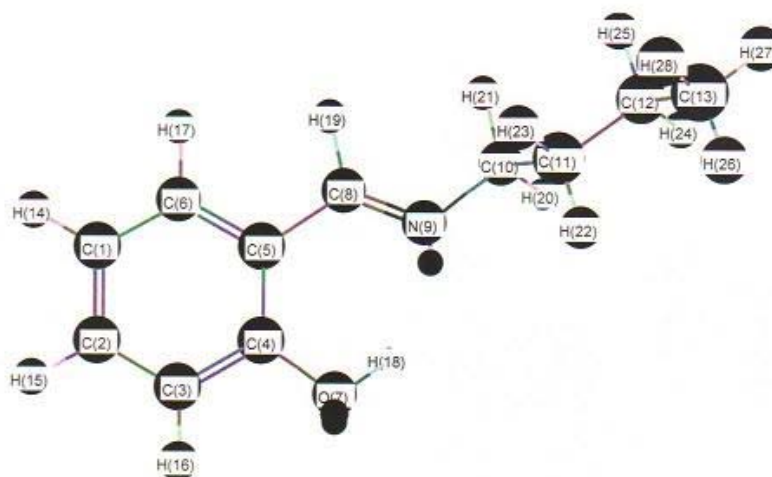


Fig. 2 : Three-Dimensional structure of Salicylidene-n-butylamine.

To find which of these factors determines the K-value of the complex, a multiple regression equation was performed by SPSS program relating K values with ChN, ChO, ChC, S, (O-N dist), dh1 and dh2, the equation was:

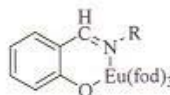
$$K = -1288.806 - 1653.722\text{ChN} - 40.197\text{ChO} - 914.860\text{ChC} + 507.207 (\text{O-N dist}),$$

with $R = 0.997$, $R\text{-square} = 0.995$.

According to this equation, the factors affecting K-values are: ChN, ChC, ChO, and O-N dist. The increase of ChN means the more availability of the lone pair of electrons, while the increase of ChO which has a lower affecting weight in K-value (in addition to the more available oxygen electron pairs) will lead to more attraction toward the hydrogen of the hydroxyl group which decreases the possibility of the intra-molecular hydrogen with the nitrogen electron pair. This facilitates the $\text{Eu}(\text{fod})_3$ interaction with nitrogen or nitrogen and oxygen atoms and thus increases the K-value of the complex. This is again supported by the O-N dist increase with their moderate affecting weight.

CONCLUSION

As a result it can be concluded that salicylidene-aliphatic amines form 1:1 charge transfer complexes with $\text{Eu}(\text{fod})_3$ and the complexation occur either through the lone pair of electrons of nitrogen or together with the lone pair of oxygen of the hydroxyl group of salicylidene part of the Schiff-base as suggested by the following structure of the complex.



REFERENCES

- Al-Rawi, J. M. A. and Saleem, L. M. N., 1989. ^{13}C NMR studies of cis-trans Isomerization of N-Benzylidene propyl and substituted Aryl-Amines Induced by LSR, *Magn. Res. Chem.*, 27, pp.540-543.
- Benesi, H.A. and Hildbrand, J.H., 1949. Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, *J. Am. Chem. Soc.*, 71, 2703 (1949).
- El-bayoumi, M. A.; El-Aasser, M., and Abdul-Halim F., 1971. Electronic spectra and structures of Schiff-bases, *J. Am. Chem. Soc.*, 93, 3, pp.586-590.
- Saleem, L. M. N., 1982. Trans-cis Isomerization of Schiff-bases (N-Benzyl-deneaniline) on addition of Lanthanide shift reagents, *Org. Magn. Res.*, 19, pp.176-180.
- Saleem, L.M.N. and Omar, A. O., 1994. ^1H NMR study of Benzylidene anilines with LSR, *J. Educ. and Sci.*, 19, pp.45-54.
- Saleem, L. M. N. and Al-Razzak, A. Y. A., 1996. Study of the Interaction of Benzylidene anilines with LSR in different solvents by U.V. Spectroscopy, *Iraq. J. Chem.*, 21, pp.57-62.
- Saleem, L. M. N. and Al-Razzak, A.Y. A., 1999. Study of the Interaction of Cinnamylidene anilines with LSR in different solvents by U.V. Spectroscopy, *Raf. J. Chem.*, 10, 1, pp.12-16.
- Saleem, L. M. N. and Al-Razzak, A. Y. A., 2000. ^1H NMR study of Cinnamylideneanilines with lanthanide shift reagents, *Raf. J. Sci.*, 11, 3, pp.8-14.

- Saleem, L. M. N.; Sulaiman, S. T. and Al-Razzak, A.Y. A., 2001. Thermodynamic study of the Interaction of Benzylidene-aminopyridene derivatives with $\text{Eu}(\text{fod})_3$ in CCl_4 , Raf. J. Sci., 12, 63-71.
- Sulaiman, S. T.; Saleem, L. M. N. and Authman, A. S., 1993. The thermodynamic behavior of the Interaction some Benzylideneaniline derivatives with $\text{Eu}(\text{fod})_3$, Iraq. J. Chem., 18, 2, 109-113.
- Sulaiman, S.T.; Saleem, L.M.N. and Authman, A.S., 1997. Interaction of some Benzylidene and Cinnamylidene aliphaticamine with LSR., Iraq. J. Sci., 38, 279-289.
- Sulaiman, S. T.; Saleem, L. M. N. and Authman, A. S., 1998. Thermodynamic study of the Interaction of Cinnamylideneaniline derivatives with $\text{Eu}(\text{fod})_3$ in acetonitrile and n-heptane, Iraq. J. chem., 24, 1, 49-53.