وزارة التعليم العالي والبحث العلمي
جامعة ميسان

الرقم الدولي : ٦٦٢٢-١٨١٥

مجلة أبحاث ميسان

مجلة علمية محكمة نصف سنوية
تصدرها عمادة كلية التربية

المجلد : ٨ العدد : ٦ السنة :

مجلة أبحاث ميسان

((مجلة علمية محكمة نصف سنوية تصدرها عمادة كلية التربية في جامعة ميسان))

حاصلة على الترقيم الدولي ١٨١٥ - ٦٦٢٢

العدد السادس عشر

المجلد الثامن

تعنون المراسلات كافة إلى: السيد سكرتير التحرير

العنوان: جامعة ميسان / كلية التربية / طريق الكحلاء .

البريد الالكتروني:najim_14@yahoo.com

الفاكس:٣١٨٦٧٦ – الهاتف: ٣١٨٦٧٦ و ٣١٥٣١٦

التصحيح اللغوي : أ.م.د. عبد الواحد خلف وساك

رقم الإيداع في دار الكتب والوثائق ببغداد ٨٦٩ لسنة ٢٠٠٥

Relationships between Electrical Conductivity and Electronic Properties for Schiff-base ligands Using Molecular Modeling and (QSPR) Techniques

Kawkab A. Hussain
Methem Najim Abood
Sadiq M. Hasan
College of Education
University of Basrah.

Abstract:

This study presented QSPR investigation on 12 Schiff-base ligands that have Electrical conductivity properties. The geometries of the compounds were optimized first at level (MM+) by molecular mechanics force field theory and then at level (MINDO) by semi- empirical theory. Quantitative Structure – Property Relationship (QSPR) have been established of 12 schiff-base compounds to correlate and predict Electrical Conductivity properties values. Linear multiple regression analysis were used to generate the equation that relates the structural features to the Electrical Conductivity properties. The results show good models with three and four parameters linear equation with R^2 value of 0.873 and 0.885 respectively, which indicate that these parameters D.M, T.E, C=N STR, LUMO,E.GAP , play an important role in effect on Electrical Conductivity properties.

Keywords. Schiff-base Lignds, Electrical Conductivity properties, (QSPR) Model.

Introduction

Schiff-bases are important class of ligands in coordination chemistry and have pharmacological as well as physiological activities.1-3 As well they are analytical reagents for the spectrophotometer determination of metal ions. Schiff base have broad applications as catalysts in chemical and petrochemical industries (2, 3) and in biological processes (4). The electrochemical determination of Schiff base and other

Ligands using various electrode systems, attain prominence in recent years

Quantitative structure – property relationship (QSPR) study is an important section in computational chemistry and uses frequently for predicting physico - chemical and biological activity of organic compounds. To establish the relation between structural characteristics of molecule and its properties the mathematical methods can be used. (5=).Multiple linear regression (MLR) is one of the mathematical methods which have an extent application. This method is useful when there is not any interaction between descriptors and their relation with linear defined activity(6=). The basic strategy of

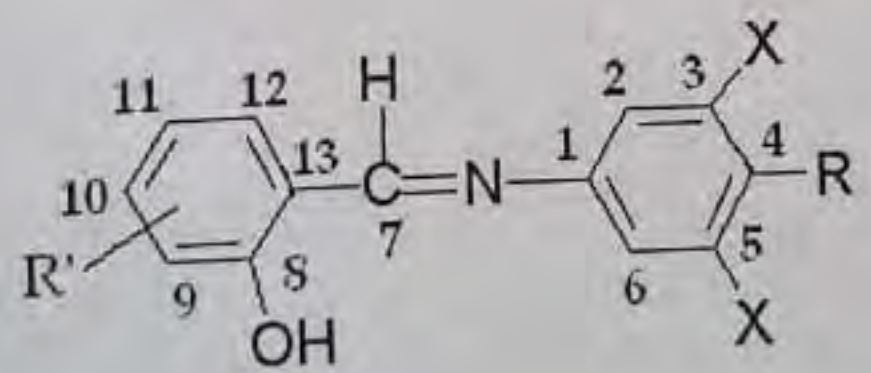
QSPR is to find the optimum quantitative relationship, which can then be used for the predication of the properties of molecular structures including those unmeasured or even unknown. QSPR has become more attractive for chemists with development of new software tools, which allowed them to discover and to understand how molecular structure influences properties, and very importantly, to predict and design the optimum structure. QSPR equations are commonly used to predicted spectroscopic, chromatographic and other analytical and industrial properties of compounds(7-8=).
In this paper a theoretical technique has been discussed by which the electrical conductivity of Schiff-base can be measure prior to their synthesis. This technique shall reduce the coast, time and efforts. In this work we demonstrate the usefulness some of the parameters in deriving predictive QSPR models. The relation between the electrical conductivity and quantum chemical calculation parameters, E_{HOMO}, E_{LOMO}, dipole moment,(C.Charge, N-Charge), Heat of formation, Energy Gap ΔE, C=N STR, C=N Length was investigated. To know the electrochemical behavior of Schiff base compounds, and to find out the effect of various the structural, chemical, physical and other properties of a schiff-base compounds understudy on experimental electrical conductivity.

Modeling and Geometry Optimization

Theoretical calculations were performed on hyperchem program version 7.5, running on a Pentium V PC-CPU 3400GHz. The geometries of the four compounds were optaimized first at level (MM+) by molecular mechanics force field theory and then at level (MINDO) by semi- empirical theory(9).

Experimental

The experimental electrical conductivity data of 12 compounds under study has been taken from reference (10). Structures of these compounds and shown in Figure.1



	1	2	3	4	5	6	7	8	9	10	11	12
R	Me	Me	Me	Me	Br	Br	Br	Br	OH	OH	OH	OH
R'	9-OMe	9-OH	10-OH	9,10-OH	9-OMe	9-OH	10-OH	9,10-OH	9-OMe	9-OH	10-OH	9,10-OH
X	H	H	H	H	H	H	H	H	t-Bu	t-Bu	t-Bu	t-Bu

Figure 1. Molecular structure of Schiff-base used in the present study

Results and Discussion

All conformers generated for each structure were analyzed in conformational geometry panel and the lowest energy conformer of each structure was selected, transferred to a database viewer to compute various physicochemical properties utilizing the QSAR descriptors module. The descriptors, which were significant for experimental data, were selected by QSAR-contingency module. To establish the statistical correlation, the physicochemical parameters were taken as independent variables and conductivity as dependent variable.

The model of QSPR study has been build up with help of the descriptors E_{HOMO}, E_{LOMO}, dipole moment(D.M), C-Charge, N-Charge, Heat of Formation, Energy Gap(ΔE),vibration of C=N STR, C=N Length was investigated. All these values for descriptors have been calculated with help of MINDO method Table 1. The data were transferred to statistical program (DATAFIT) and multiple liner regression (MLR) analysis was performed to generate the statistically significant QSPR models between conductivity of compound under study and physicochemical properties. The best model was selected on the basis of statistical parameters viz observed correlation coefficient (R), sequential Fischer test (F), and standard error of estimate (S), were used to evaluate the obtained QSPR models.

. Table 1. Calculated physico-chemical parameters of the compounds

AP V	LUMO eV	HOMO eV	D. M (Deby)	Heat of formation	E_T	C - CHARGE	N- CHARGE	C=N angstrom
212	-0.1841	-8.8053	2.842	-26.6150	-68737.3125	0.149	-0.22	1.289
405	-0.2690	-8.9096	1.625	-3336.2170	-65141.9101	0.16	-0.229	1.286
577	-0.3383	-8.7960	1.155	-35.5938	-65143.1914	0.151	-0.255	1.292
414	-0.2683	-8.9097	1.622	-34.3110	-65141.9101	0.136	-0.233	11.29
641	-0.4098	-8.974	4.565	-15.9529	-72818.4375	0.167	-0.234	1.286
960	-0.4119	-9.0080	1.333	-23.8274	-69223.2109	0.144	-0.237	1.29
524	-0.4889	-8.9413	1.744	-25.1506	-69224.5390	0.162	-0.264	1.293
961	-0.4119	-9.0080	1.333	-23.8274	-69223.2109	0.144	-0.237	1.29
461	-0.3927	-8.9389	2.635	-59.9859	-101382.2891	0.133	-0.233	1.291
972	-0.3325	-8.9298	2.258	-69.0909	-97788.2968	0.135	-0.231	1.291
920	-0.3998	-8.7918	2.087	-70.3754	-97789.5781	0.152	-0.255	1.293
236	-0.4205	-8.8442	1.607	-116.8977	-105226.0391	0.144	-0.245	1.292

Definition of Descriptors Used in This Study.
Energy. GAP=Different between HOMO and LUMO is energy gaps in eV
LUMO= The energy of Lowest Unoccupied Molecular Orbital in eV
HOMO= The energy of Highest Occupied Molecular Orbital in eV
D.M= Dipole moment , debyes
Heat. E= Heat of Energy in Kcal/mol
Length of C=N = Length Bond of the Azomethin Group (C=N) in Angstrom.
E_T = Total Energy in Kcal/mol

Several combinations of independent variables were firstly attempted using three variables (one representative from each property),for individual models, and then, more variables, and then more variables were added in order to optimize the statistical values but not more than four independent variables were used. The best model derived from the (MLR) analysis was used to predictive the conductivity of compounds understudy. The resulting parametric models are depicted in Eq. 1-4, along with statistical parameters of the regression.

The first model when depend on only one parameter [D.M] gave poor model with correlation coefficient R^2 values for this model of 0.36, as equation 1

Model-1

$$Y= -1.3497\ D.M + 17.45672 \quad \ldots\ldots\ldots\ldots (1)$$
$R^2= 0.367$ F= 5.811 S= 1.754

While the correlation coefficient R^2 increase when using the two parameters [D.M+T.E] and become 0.57 (equation 2).

Model-2

$$Y= 13.01759- 6.00511\ T.Energy- 1.49439\ D.M \quad \ldots\ldots\ldots (2)$$
$R^2=0.578$ F= 6.170 S= 1.510

On other hand when three parameters[D.M+T.E+ C=N STR] are used in the model equation, the correlation coefficient R^2 value rised to 0.767 and 0.830 respectively. Eq. 3and Eq. 4.

Model-3

Y= -163.7584 E.GAP- 15.40325 HOMO -15.43708 C-CHARGE C=N+34.07094.....Eq. (3)

R^2= 0.767 F= 7.702 S= 1.231

Outlier = No. 9

Y= 9.12232E.GAP – 3.77169D.M- 1.18885 T.Energy- 65.5220 ……Eq. (4)

R^2=0.830 F= 11.394 S= 0.99

Outlier = No. 5

Model -4. While when four parameters[T.E, D.M, E.GAP, C=N STR] or [T.E, D.M, LUMO, C=N STR] are used in the model equation the correlation coefficient R^2 value rised to 0.873 and 0.885 respectively. Eq. 5and Eq. 6.

The percentage of correlation coefficient R^2 increased dramatically from one parameter to four parameters Eq. 5and Eq. 6, which show very good correlation coefficient R^2 .

Model-4

Y= -1.186233 X10^{-4}T.Energy-3.7983D.M-1.27030E.GAP+0.19442$C=N_{STR}$-352.25203...Eq (5)

R^2=0.873 F=12.098 S= 0.937

Y= -1.12671X 10^{-4}T.Energy-3.63353D.M-3.06696LUMO+0.18079 $C=N_{STR}$-337.70741…Eq(6)

R^2=0.885 F= 13.468 S=0.894

Relations between descriptors and experimental electrical conductivity can be seen in Table 2.

Table 2. Predicated Experimental data

Sr. No	Conductivity (obsd) S cm^2 mol^{-1}	Conductivity (Pred) Eq-1 R^2=0.36	Eq-2 R^2=0.57	Eq-3 R^2=0.76	Eq-4 R^2=0.83	Eq-5 R^2=0.87	Eq-6 R^2=0.88
1	11	13.62	12.89	12.21	10.57	11.35	11.03
2	14	15.26	14.50	11.72	14.91	14.53	14.38
3	14	15.89	15.20	14.26	15.02	14.82	14.70
4	15	15.26	14.50	15.56	14.93	14.55	14.40

5	12	11.29	10.56	12.74	0utlier	11.93	12.03
6	16	15.65	15.18	16.54	16.09	16.49	16.63
7	14	15.10	14.56	14.78	13.23	12.86	13.28
8	17	15.65	15.18	16.54	16.09	16.49	16.63
9	13	13.90	15.16	Outlier	14.55	14.16	14.29
10	17	14.40	15.51	16.79	16.01	15.71	15.64
11	15	14.63	15.77	15.05	14.78	14.82	14.79
12	18	15.28	16.93	16.68	17.77	18.23	18.13

Conclusion

The quantum chemical calculations can be successfully used for the prediction of electrical conductivity of Schiff-base understudy was correlated using QAPR models. Schiff-base compounds can be modeled by using quantum chemical calculations. The model depending on the eq. 6. is the best produced model with very good statistical fit as evident from its $R^2 = 0.885$, $F = 13.468$ and $S2 = 0.894$. It is evident from the results that the electrical conductivity of the Schiff-base is influenced mainly by total energy, dipole moment, the energy of lowest unoccupied molecular orbital and vibration of C=N str.

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العلاقة بين التوصيلية الكهربائية و الخواص الالكترونية لقواعد شف باستعمال الموائمة الهندسية وتقنيات QSPR

كوكب علي حسين العلي
ميثم نجم عبود
صادق محمد حسن
كليه التربية -جامعة البصرة

الملخص :
الدراسة قدمت العلاقة التركيبة ل ١٢ من ليكاندات قواعد شف التي تمتلك خواص توصيلية كهربائية. الموائمة الهندسية لهذه التراكيب أنجزت أولا بطريقة (+MM)ومن ثم أكملت الموائمة الهندسية بطريقة الشبه تجريبية MINDO. العلاقة بين الخواص والتركيب أجريت إل ١٢ من مركبات القاعدة شف لتنبأ بقيم خواص التوصيلية الكهربائية... التحليل الخطي استخدم لاختيار الموصوفات لتكوين معادله ترتبط بالمميزات التركيبية لخواص التوصيلية الكهربائية. النتائج أظهرت أفضل موديل الذي يحتوي ثلاثة وأربعة متغيرات مع قيمه جيده ل R^2= 0.873, 0.885 على التوالي والتي أكدت بأن هذه المتغيرات D.M, T.E, C=N STR, LUMO,E.GAP.لها دورا مهما في التأثير على خواص التوصيلية الكهربائية .