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Der Pharmacia Lettre, 2012, 4 (6):1826-1831
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Quantum Chemical QSPR Study of The Best Parameters Influences On Heat Transition (ΔH) for Schiff-base Compounds

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ABSTRACT

Quantitative Structure-Property Relationship (QSPR) analysis to heat transition (ΔH) of 11 Schiff-base compounds have been conducted. The study was done by using molecular modelling of Schiff-base compounds. The calculation was performed by the DFT method at B3LYP/6-31G (d) level of theory. The relationship analysis between heat transition (ΔH) and physicochemical properties of Schiff-base compounds was done by MLR analysis, with heat transition (ΔH) as dependent variable and 8 independent variables to generate the equation that relates the structural features to the heat transition (ΔH) properties. The results show good models with five and six parameters linear equations. The best model predicted in this study is the six parametric regression equation (Eq. 4) In which the descriptors [T.E, D.M, HOMO, V.W.V, LUMO and HARDNESS- η] are included, with values of R^2=0. 976, F= 27.187 and S=5. 902, which indicate that these parameters, play an important role in effect on heat transition (ΔH) properties.

Keywords: Sciff-base, Heat transition (ΔH) properties, (QSPR) Model.

INTRODUCTION

Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition, and replacement reactions [1]. Moreover, Schiff bases are also known to have biological activities such as antimicrobial [2], antifungal [3], antitumor [4], and as herbicides [5]. Schiff bases have also been employed as ligands for complexation of metal ions [6]. On the industrial scale, they have wide range of applications such as dyes and pigments [7]. Experimental measurements of some thermodynamic parameters involve experimental difficulties and they are not always feasible, and the corresponding methods possess real drawbacks [8]. Consequently, it is necessary to resort to a theoretical calculation of these parameters. This option is now accessible because an important, fruitful and current field of research in contemporary chemistry is the model and prediction of physical-chemistry properties of molecules [9]. This kind of study is based on the paradigm that physical-chemistry properties and biological activities are dependent on molecular structure. As a consequence, one of the most important points in such research is the selection of adequate descriptors containing the information stored in the molecular structure [10].

Quantitative structure–property/activity relationships(QSPR/QSAR) are tools to estimate physico-chemical and biochemical parameters and reduce the coast, time and efforts [11-14]. (QSPR/QSAR) 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. 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[15-17]. Most QSAR/QSPR treatments utilize a program to calculate descriptors and then try to select a small number of descriptors in a purely empirical fashion to form an equation which allow chemists to elucidate and to understand how molecular structure influences properties, this helps researchers to predict and prepare structures

with optimum properties. In this paper sequential multiple regression analysis (MLR) method was applied in quantitative structure–property relationships (QSPR) for modeling the relationship between heat transition of 11 schiff-base as described in Ref [18] and their structural descriptors and predicated it theoretically.

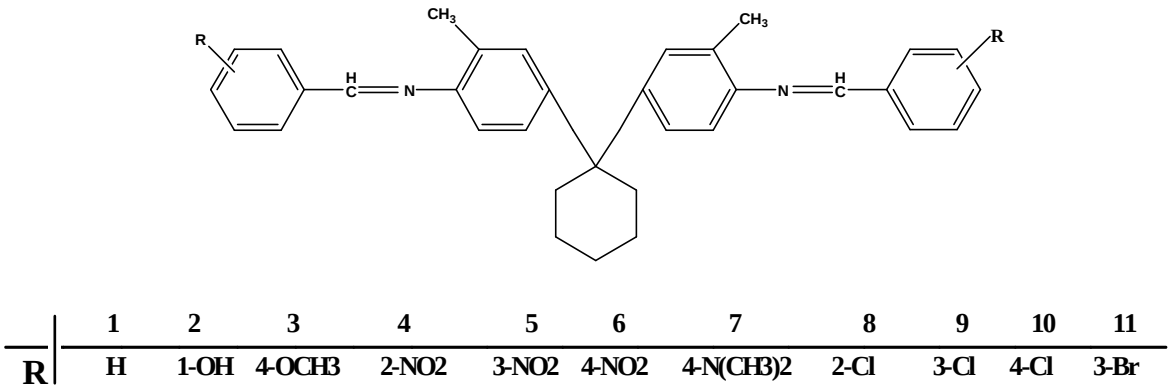
Modeling & Geometry Optimization

The quantum chemical calculations were performed for 11 compounds understudy with the firefly QC package[19]. Geometrical optimizations were carried out using Density Functional Theory (DFT) method at B3LYP/6-31G(d) level of theory. B3LYP refers to the combination of functional hybrid exchange of Becke [20]. With functional correlation gradient of Lee and Yang[21].

MATERIALS AND METHODS

Experimental

The experimental heat transition (ΔH) data of 11schiff-base compounds under study has been taken from reference[18]. Structures of 11 sciff-base compounds shown in Figure.1



	1	2	3	4	5	6	7	8	9	10	11
R	H	1-OH	4-OCH3	2-NO2	3-NO2	4-NO2	4-N(CH3)2	2-Cl	3-Cl	4-Cl	3-Br

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

RESULTS AND DISCUSSION

The relationship between heat transition (ΔH) and various descriptors (Physiochemical and alignment-independent) were established by sequential multiple regression analysis (MLR) in order to obtain QSPR models. The best multilinear regression (BMLR) procedure [16] was used to find the best correlation models from the selected noncollinear descriptors. The descriptors Table 1., which were significant for experimental data, were selected by QSPR-contingency module. To establish the statistical correlation, the physicochemical parameters were taken as independent variables and heat transition as dependent variable. The best model was selected on the basis of statistical parameters viz observed with high correlation coefficient (R), sequential Fischer test (F), and low standard error of estimate (S), were employed to judge the validity of regression equation and evaluate the obtained QSPR models[17&22].

Table 1. Calculated physico-chemical parameters of the compounds

No.	T.E	D.M	HOMO	χ	LUMO	η	ΔE	V.W.V
1	-1425.57	3.482327	-5.24912	3.298043	-1.34697	1.95107	3.902143	467.66
2	-1576.01	5.539046	-5.12394	2.810957	-0.49797	1.944265	3.88853	484.503
3	-1654.63	5.158827	-5.21646	8.489965	-1.2735	1.97148	3.94296	519.135
4	-1834.54	3.557414	-5.2464	3.744315	-2.24224	1.50208	3.00416	514.944
5	-1834.58	6.546461	-5.543	3.998744	-2.45449	1.544255	3.08851	516.12
6	-1834.58	4.358019	-5.68722	4.2831	-2.87898	1.404118	2.808237	515.126
7	-1693.5	5.538527	-5.05864	3.118449	-1.17826	1.940187	3.880374	560.71
8	-2344.03	4.659798	-4.91441	3.383761	-1.85311	1.527937	3.055862	490.465
9	-2344.77	2.978836	-5.2981	3.469474	-1.64086	1.8286195	3.657239	495.866
10	-2344.77	0.79332	-5.45048	3.553834	-1.65719	1.8966485	3.793297	495.759
11	-6567.87	2.718227	-5.33892	3.47356	-1.60821	1.865355	3.73071	504.226

Definition of Descriptors Used in This Study.

ΔE=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., **V.W.V** = VANDER WALES Volume in Ang^3 according the Facio program version 14.2.4.[12]., **T. E** = Total Energy in Kcal/mol., **χ**=ELECTRONAGATIV, **η**= HARDENSS.

The next most important descriptors involved in the QSPR models are the HOMO energy, LUMO energy, HOMO-LUMO energy gap(ΔE), Dipole moment, Vander Wales Volume, Total Energy, ELECTRO, Hardenss can be directly related with experimental data of heat transition (ΔH). The five- and six- descriptor correlations of the heat transition (ΔH) were given in eqs (1-4) respectively and the resulting parametric models are depicted in figures. 2-6, along with statistical parameters of the regression[23-25]. The highest value for R^2 obtained in five- descriptor correlation (R^2 = 0.933) suggests the following model:

This is the first model when depend on only five- descriptor [D.M, HOMO, T.E, LUMO and ΔE.] gave good model with correlation coefficient R2 values for this model of 0.933, as eq 1.

ΔH=-8.4785+/-8.1925D.M+114.8786+/-83.1038HOMO+9.05006X10-3+/-8.4281X10-3T.E-61.5341+/-56.5599 LUMO +76.8933+/-71.5059**Δ**E+325.729+/-363.6604…….. **Eq---1**

Statistical characteristics of the obtained equation:
R^2=0.933 F =14.090 S=8.785

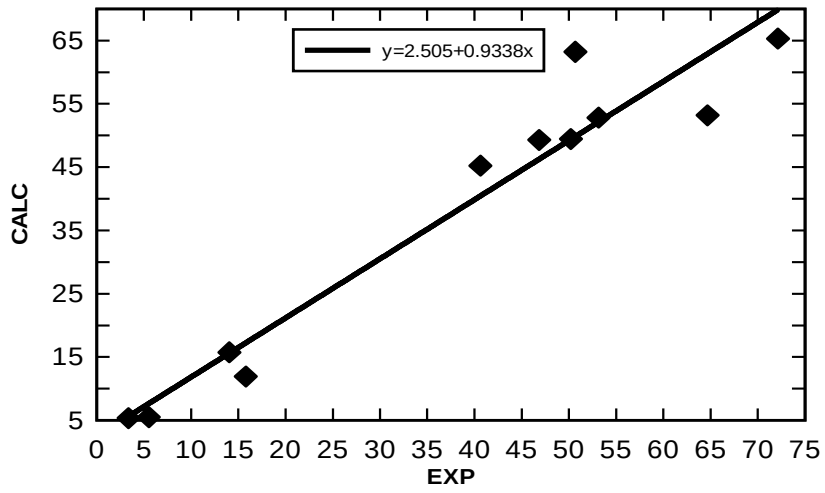


Fig. 2, show the relationship between the experimental ΔH data and predicted ΔH by this model.

Fig 2. Present the relationships between experimental ΔH and predicted ΔH by Eq 1.

While in the eq.2, five descriptors, the good correlation coefficient R^2 obtained when replacement the descriptors ΔE by Hardness, on the other hand in the eq 2. It can be seen decrease the standard error comparable with eq 1.

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ΔH=-8.4785+/-8.192D.M+114.8776+/-83.102HOMO+9.05X10-3+/-8.428X10-3T.E-61.5342+/-56.559LUMO+ 153.787 +/-143.0113HARDNESS+325.7214+/-363.6589 ……..**Eq—2**

Statistical characteristics of the obtained equation:
R^2 = 0.933 F =14.091 S = 8.784

Fig. 3, show the relationship between the experimental ΔH data and predicted ΔH by this model.

With six descriptors eq 3.. of the heat transition (ΔH). of Schiff-base compounds increases with the descriptors { T.E, D. M, HOMO, ΔE, LUMO, and V. W. V]. in this eq 3. depends on six descriptors gave very good model with change in the correlation coefficient R^2 values to 0.976, high sequential Fischer test (F) and the low standard error of estimate (S).

ΔH=9.4109X10-3+/-6.496x10-3T.E-10.7079+/-7.375D.M+103.6107+/-66.679HOMO+61.3724+/-61.089**Δ**E-48.2862+/-49.083LUMO+0.2544+/-0.4404 V.W.V+224.6104+/-329.385…… **Eq-3**

Statistical characteristics of the obtained equation:

R^2 = 0.976 F =27.186 S = 5.903

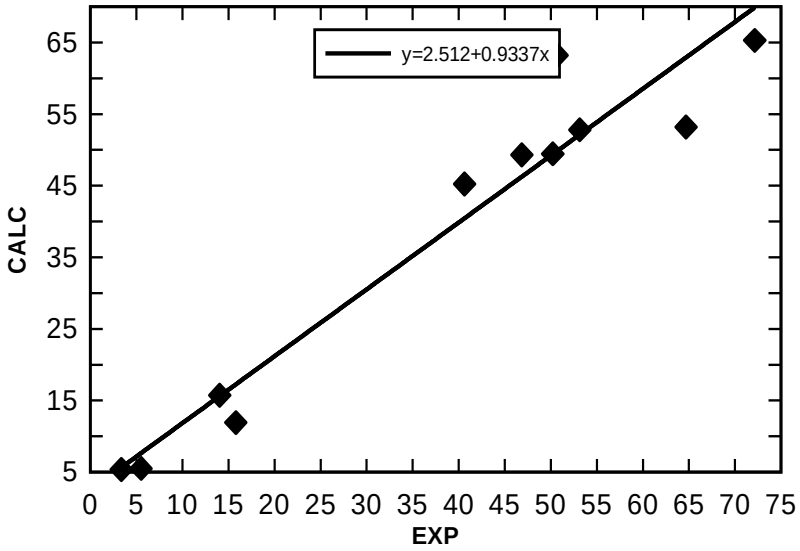

Fig 3. Present the relationships between experimental ΔH and predicted ΔH by Eq 2.

Fig. 4, show the relationship between the experimental ΔH data and predicted ΔH by this model.

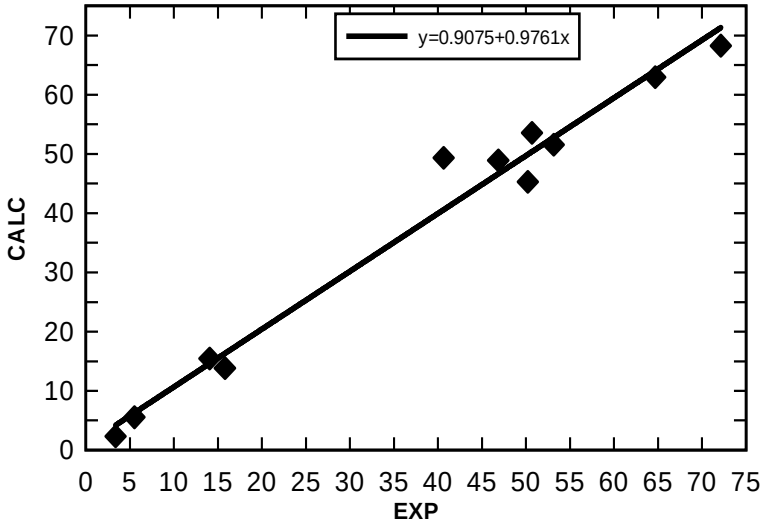

Fig. 4. Present the relationships between experimental ΔH and predicted ΔH by Eq 3.

In eq 4. Also when using six descriptors [T.E, D.M, HOMO, V.W.V, LUMO and HARDNESS] by replacement the ΔE in eq 3. by HARDNESS in eq 4**.** As seen from this resulting in a very minor improvement of the correlation coefficient, standard error and of the sequential Fischer test (F), in contrast with eq 3. This indicted that these descriptors have positive effect on heat transition (ΔH) properties of Schiff-base compounds understudy.

ΔH=9.411X10-3+/-6.496X10-3T.E-10.7079+/-7.3757D.M+103.61+/-66.677HOMO+0.2544+/-0.4405V.W.V-48.2863+/-49.082LUMO+122.746+/-1221HARDNESS+224.6041+/-329.375... ...**Eq 4.**

Statistical characteristics of the obtained equation:
R^2 = 0.976 F =27.187 S = 5.902

Fig. 5, show the relationship between the experimental ΔH data and predicted ΔH by this model.

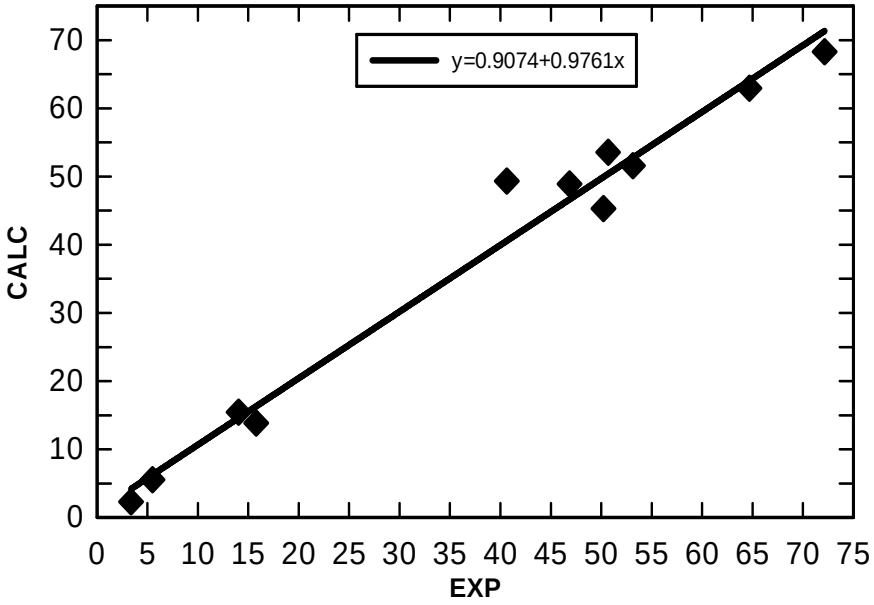

Fig 5. Present the relationships between experimental ΔH and predicted ΔH by Eq 4.

CONCLUSION

The QSPR mathematical models consist of multiple regressions taking into account only the influential descriptors. Using the linear model, multiple regressions were performed between some characteristic temperatures of heat transition (ΔH) and some quantum chemical parameters/descriptors. The study indicated that heat transition (ΔH) for Schiff-base compounds can be modeled. The values of R^2 for the QSPR models Eqs, 1-4 range from 0.933-0.976, the values of S range from 8.785-5.902, and the values of F range from 14.090 -27.187. The values of R^2, S and F suggest that the QSPR models Eqs. 1-4 are predictive and validate. From all the results the Eq 4. have smaller the value of S and the larger the value of F, the better the QSPR model. As well as the heat transition (ΔH) increases with increasing the descriptors understudy including [T.E, D.M, HOMO, V.W.V, LUMO and HARDNESS] Eq 4., Finally, the good agreement between experimental and predicted values using MLR model, confirm its validity and showed insignificant role in the a predict the data of the heat transition (ΔH). This study may be helpful for the chemists and researcher to understanding thermodynamic parameters (heat transition (ΔH)) of Schiff-base compounds .

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