Proceedings of Science and Mathematics
Faculty of Science, Universiti Teknologi Malaysia
Vol. 14, 2022, page 91-99

Investigation of Nonlinear Optical Response of Metal Complexes via Quantitative Structure-Activity Relationship Method

Lee Yang Ning and Fazira Ilyana Abdul Razak*
Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Johor, Malaysia
*Corresponding author: yangninglee@graduate.utm.my

Abstract
A quantitative structure–activity relationship (QSAR) is formed by attempting to construct a quantitative relationship between the effects (which is activity) and the chemistry (which is structure) of a set of compounds. It is a quantitative explanation of the function of structure in governing effects, i.e. that a fragment or sub-structure could result in a specific activity. Nonlinear optics (NLO) is the study of phenomena caused by changes in the optical characteristics of materials caused by light. When light interacts with a nonlinear optical material, it creates new optical fields with different properties (such as phase, frequency, amplitude, polarization, path and others). To develop NLO materials, time consumption and cost would be high because in order to see whether a compound possesses good NLO properties, one must go through many steps of procedure. Hence, a computational method through QSAR, we can predict whether a certain compound is a good NLO material without many steps of procedure. In this study, 9 metal compounds are geometrically optimized using Gaussian16 and then used for QSAR. Results from Gaussian16 showed that Structure 4 is the most stable compound with the lowest optimization energy of -0.7132 a. u. and Structure 6 has the lowest band gap energy with 0.16354 eV. The highest dipole moment is shown by Structure 2 with 11.85 D and Structure 5 shows the lowest dipole moment with 0.00 D. Based on QSAR, band gap energy parameters shows the biggest contribution to NLO response for metal complexes with R^2 of 0.445. With that being said, more research is still needed in this area of study to have a better understanding and to obtain a more accurate result.

Keywords: Nonlinear optics, metal complexes, quantitative structure-activity relationship

1. Introduction

Nonlinear optics (NLO) is the study of phenomena caused by changes in the optical characteristics of materials caused by light. When light interacts with a nonlinear optical material, it creates new optical fields with different properties (such as phase, frequency, amplitude, polarization, path and others [1]. Lasers that provide the high-intensity electromagnetic fields required for NLO motivates the observation of NLO occurrences after the laser's invention in 1960 [2].

NLO-efficient materials continue to pique people's imagination, with a slew of applications driving the research forward. Hence, simplified methods that are easily accessible are needed to study NLO properties to have more researches on the said subject. The importance of NLO properties is NLO materials were employed as important materials in photonic communications, which transmit data using light rather than electrons. NLO materials have been widely used in industry, national defence, medicine, and research since the development of laser technology. For these uses, a variety of organic compounds were utilised [3].

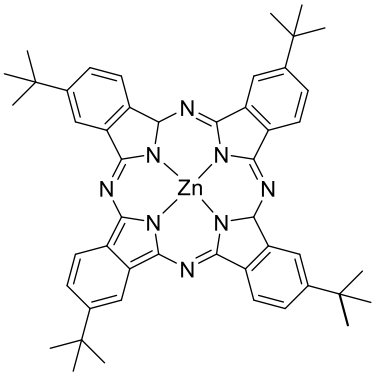
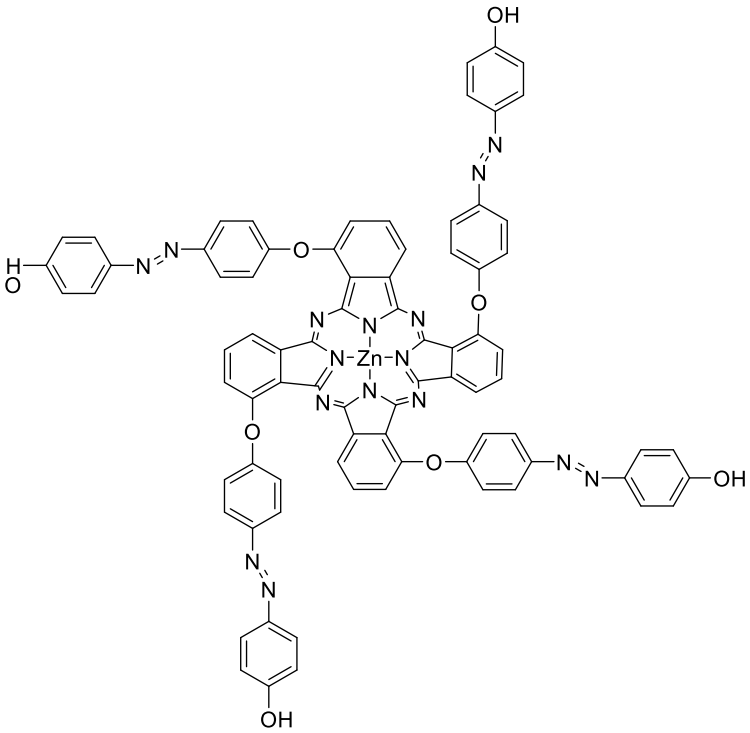
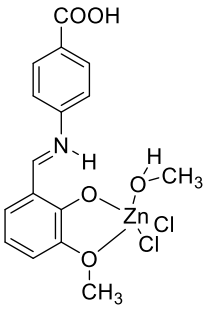
The quantitative structure-activity relationship (QSAR) is the most widely used theoretical tool for predicting how a compound's biological activity, physical, chemical, and technical qualities are influenced by its chemical structure [4]. Scientists can now predict bioactivities and physical or chemical attributes of a series of freshly developed compounds before deciding whether or not to synthesis and test them using this method. These predictions are based on structural traits, or molecular descriptors, that account for the majority of differences in biological activity or property of interest.

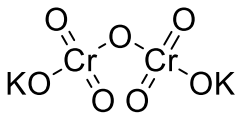
2. Methodology

2.1 Structure Identification

The experimental values for all the structures are obtained from previous works by various researchers. Table 1 below shows all the structures used for this study.

Table 1. Structure Identification

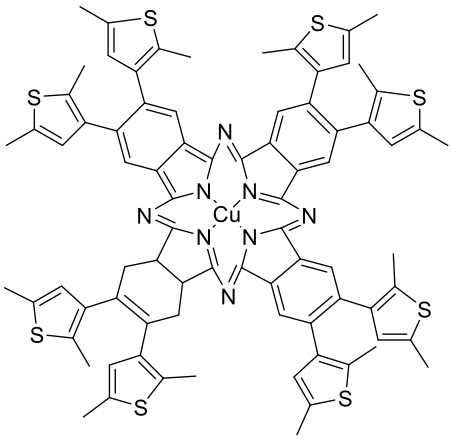
No.	Structure	Reference
1.		Kumar *et al.*, 2007
2.		Chen *et al.*, 2011
3.		Kamaal *et al.*, 2021

4. 

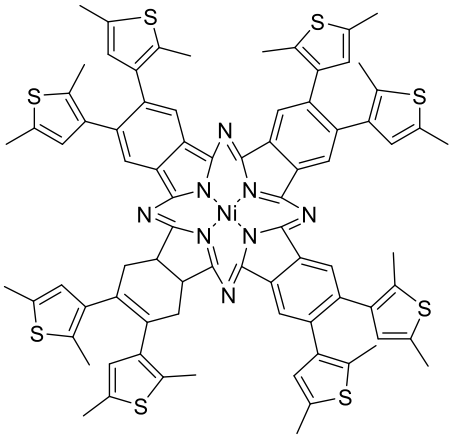
Thilak *et al.*, 2013

5. 

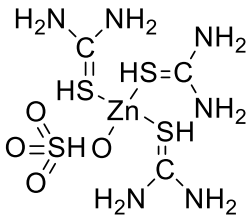
Maldonado *et al.*, 2020

6. 

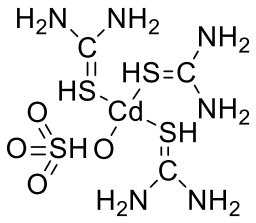
Chen *et al.*, 2011

7. 

Chen *et al.*, 2011

8. 

Dhanuskodi *et al.*, 2011

9.		Dhanuskodi *et al.*, 2011

2.2. Gaussian16

All the structures are drawn using GaussView. Then, all the structures are optimized using the Semi-Empirical Method (SEM) with the basis set of PM6. The setting is lowered down from DFT Ab Initio B3LYP functional to the SEM due to time constraint and limited amount of high-performance computer to run the calculations. After geometry optimization, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), band gap energy, dipole moment and optimization energy are extracted for QSAR calculations. Then, all structures will be submitted for NLO calculations with the same method with additional keyword of "polar=gamma" to obtain β_{tot} values.

2.3. Z-Scan

The NLO properties which is the nonlinear refractive index (n_2) values are determined from previous works (Table 1). The Z-scan instrument used in the research from Table 1 set the wavelength in the range of 600nm to 800nm. The optimal limiting was carried out by simultaneous measurement of both incident and transmitted pulse energies with the same experimental system used for Z-scan.

2.4. Discovery Studio

The QSAR software used for this research is Discovery Studio implementing the module "calculate molecular properties" which runs on a INTEL CORE i7 processor. For $dmol^3$ calculation, the functional used is B3LYP. QSAR were run on all of the structures to obtain an equation which is the objective of the study. The method used for QSAR is Multiple Linear Regression (MLR) which is to calculate and correlate the values based on the calculated results that is obtained through Gaussian previously. After all the input are set and run using QSAR, the result gave a graph and also an equation that achieved the objectives of this study.

3. Results and Discussion

In this study, Gaussian16 software is used for geometry optimization and Discovery Studio software is used for QSAR. The basis set used for geometry optimization by Gaussian16 is the SEM with the setting of PM6. Throughout this study, 9 structures were successfully calculated (refer to Table 1).

The NLO responses measured by Z-scan instrument is used to obtain the n_2 values. The Z-scan instrument used in the research from Table 1 set the wavelength in the range of 600nm to 800nm. The n_2 values are obtained from previous works by various authors. Table 2 below shows the results.

Table 2. Experimental Results

Structure	n_2 Value (cm^2/W)
1	1.14×10^{-15}
2	3.30×10^{-16}
3	-1.35×10^{-7}
4	9.41×10^{-8}
5	3.00×10^{-16}
6	3.70×10^{-16}
7	3.40×10^{-16}
8	-5.22×10^{-8}
9	-7.71×10^{-8}

All the structures were drawn using the GaussView software. Then, the file is saved as an input file to be opened in Gaussian16. After that, calculations were run on Gaussian16 software. All the calculations were successfully calculated using Gaussian16 software with SEM and basis set of PM6. The results of the calculations along with the discussion of the results are shown below.

From Table 3, we can see that Structure 7 has the highest optimization energy with 1.0288 a. u. and Structure 4 has the lowest optimization energy with only -0.7133 a. u.. The other structure that has relatively high optimization energy would be Structure 2 because it contains 153 atoms in the compound. This shows that when there is high number of atoms, the optimization energy would be high as well. For dipole moment, Structure 2 has the highest value of 11.85 D and Structure 5 has the lowest dipole moment with the value of 0.00 D. It can also be seen that the band gap energy is obtained by subtracting the HOMO and LUMO. The highest HOMO in terms of magnitude is Structure 4 with -11.8465 eV and the lowest LUMO in terms of magnitude on the other hand is Structure 5 with -3.4093 eV. The highest band gap energy is Structure 4 with 8.1180 eV because it has the largest difference of HOMO and LUMO. The lowest band gap energy on the other hand is Structure 6 with 0.1635 eV because it has the smallest difference of HOMO and LUMO. Overall, this energy calculation highly depends on the number of atoms and geometry arrangement of the structures.

Table 3. Geometry Optimization Results

Structure	Optimization Energy (a. u.)	Dipole Moment (D)	HOMO (eV)	LUMO (eV)	Band Gap Energy (eV)
1	0.2366	6.42	-7.6162	-6.3879	1.2283
2	0.5048	11.85	-7.5792	-6.3922	1.1870
3	-0.3751	6.04	-8.3955	-6.1005	2.2950
4	-0.7133	10.33	-11.8465	-3.7285	8.1180
5	0.1963	0.00	-7.5430	-3.4093	4.1337
6	0.7382	5.96	-5.4940	-5.3304	0.1635
7	1.0288	9.45	-7.4143	-6.3027	1.1116
8	-0.2963	3.07	-6.1138	-3.8161	2.2977
9	-0.2140	7.59	-5.5114	-3.7097	1.8017

To obtain second order hyperpolarizability, β_{tot} results from Gaussian16 calculations, the equation used is:

$$\beta_{tot} = (x^2 + y^2 + z^2)^{0.5}$$

where the values are obtained from the log file of the output file [5]. The basis set used to run for NLO on Gaussian is also using SEM with PM6 but with additional keyword of “polar=gamma” is added. Table 4 shows the result obtained.

Table 4. Second Order Hyperpolarizability, β_{tot} Values

Structure	β_{tot} (x 10^{-30} esu)
1	2290.0896
2	2305.1450
3	464.0151
4	9.7953
5	-
6	1699.3825
7	521.6618
8	29.1029
9	39.5433

Based on Table 4, a pattern can be seen for the NLO results. By comparing Structures 1, 2, 3 and 8 which have the same metal, Zn but different structures, it can be seen that Structure 2 has the highest β_{tot} value due to the greatest number of aromatic rings (17) while the structure that shown the second highest β_{tot} value have the second highest number of aromatic rings (8). By comparing Structures 6 and 7 which have the same structures but different metals, it can be seen that when the metal mass increases, the higher the β_{tot} value. This hypothesis can be supported by comparing Structures 8 and 9 which also have the same structures but different metals, it can be seen that when the metal mass increases, the higher the β_{tot} value as well. Other than that, by comparing Structures 6, 7, 8 and 9, it can be seen that the lower the band gap energy, the higher the β_{tot} value. For dipole moment and β_{tot} relationship, the structure with the highest dipole moment (Structure 2) of 11.85 D also has the highest

β_{tot} of 2305.1450 while the structure with the lowest dipole moment (Structure 5) of 0.00 D does not have any β_{tot} values because Gaussian could not obtain the dipole orientation (which is needed for the calculation of β_{tot}) for a compound which has 0.00 D. Hence, it can be said that the relationship for dipole moment and β_{tot} is directly proportional.

In this study, all the geometrically optimized compounds were used for QSAR calculations. The calculations involve 4 descriptors that was individually calculated. From here, the QSAR models developed can be used for future concerns when designing NLO materials. In QSAR calculations, there are 2 steps involved which is input file preparation and QSAR simulation using MLR correlation.

Since this research is about studying the effects of conjugation, metals, band gap energy and dipole moment towards NLO response, the number of double bonds and metal mass are used to measure effects of conjugation and metals respectively while values for band gap energy and dipole moment are obtained from Gaussian16 calculations. Other than the said values, values from Table 3 and Table 4 are also used in QSAR. Table 5 below shows the values for the descriptors.

Table 5. Values of Descriptors

Structure	Number of Double Bonds	Metal Mass (g/mol)
1	17	65.38
2	47	65.38
3	7	65.38
4	4	182.19
5	2	92.91
6	33	63.55
7	33	58.69
8	6	65.38
9	6	112.41

After data input, the linear graphs alongside the equations are obtained. There are 4 descriptors that are taken into consideration which are band gap energy, metal mass, dipole moment and conjugation. All the R Square values are then put into a table below to compare which descriptor shows the highest NLO response, shown in Figure 1-4.

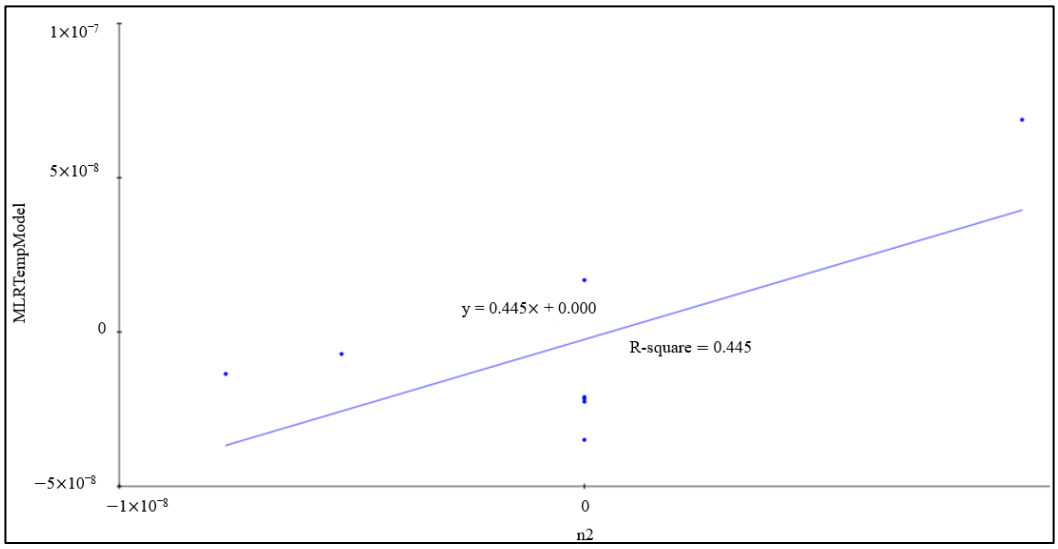


Figure 1. QSAR Analysis Plot on Band Gap Energy

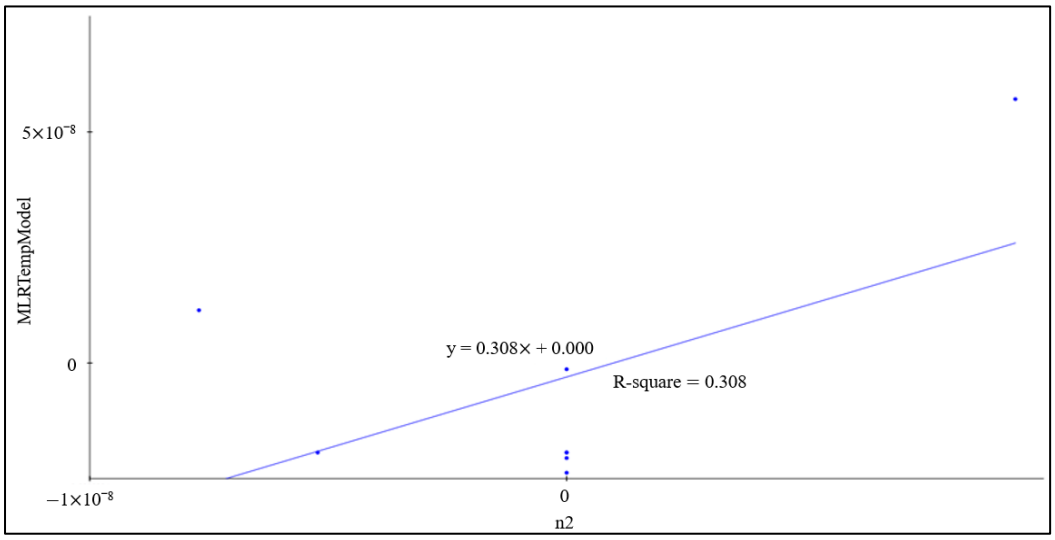


Figure 2. QSAR Analysis Plot on Metal Mass

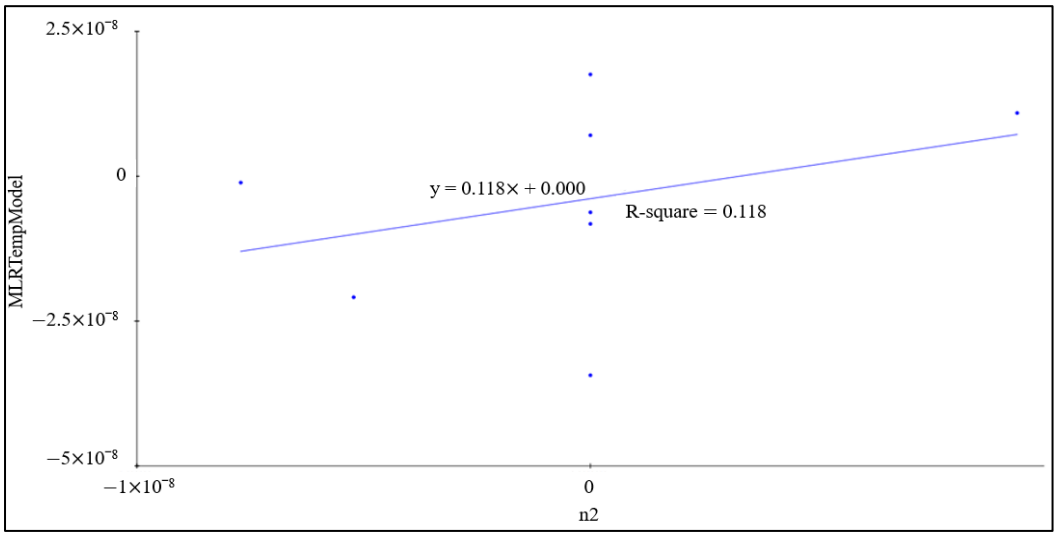


Figure 3. QSAR Analysis Plot on Dipole Moment

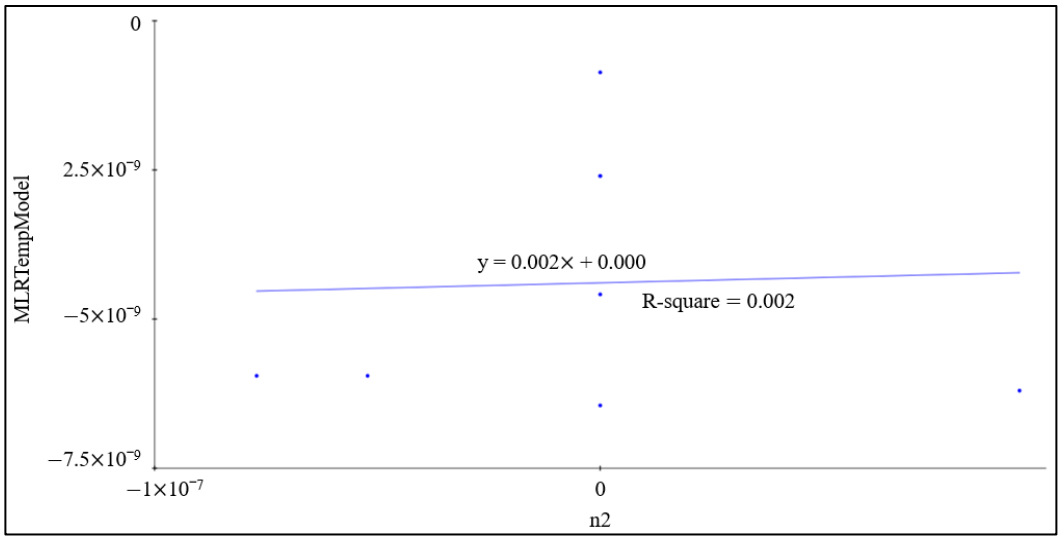


Figure 4. QSAR Analysis Plot on Conjugation

From Table 6, we can see that the effect of band gap and the effect of metal mass are the highest and the second highest towards NLO response respectively. After identifying which descriptor shows high NLO response, then among the 9 structures studied, identification of the one particular structure that shows the highest NLO response is conducted. For each of the equations, y is the NLO value.

Table 6. R Square Values

Effect	R Square	Equation
Band Gap Energy	0.445	y = 0.445x
Metal Mass	0.308	y = 0.308x
Dipole Moment	0.118	y = 0.118x
Conjugation	0.002	y = 0.002x

The experimental n_2 values varies greatly with the calculated β_{tot} values because the Z-Scan is conducted on the compounds which are in solvent phase while the calculated method is done for the compounds in gas phase. However, a positive trend could be observed as discussed below. From Table 7, it can be seen that the lowest band gap energy which is Structure 6 with 0.1635 eV has the third highest β_{tot} of 1699.3825 but Structure 2 has the highest β_{tot} of 2305.1450 even though the band gap energy is higher than Structure 6. Supposedly, the lower the band gap energy, the higher the β_{tot} but this can be explained by comparing the experimental n_2 values where it shows that Structure 6 has higher n_2 value than Structure 2. This shows that the calculated band gap energy follows the trend that low band gap energy have high NLO response. The calculated β_{tot} is lacking accuracy because SEM is used whereas GEN method is supposedly more accurate when metal complexes are involved.

Table 7. NLO Relationship

Structure	β_{tot} (x 10^{-30} esu)	n_2 Value (cm^2/W)	Band Gap Energy (eV)	Metal Mass (g/mol)
1	2290.0896	1.14×10^{-15}	1.2283	65.38
2	2305.1450	3.30×10^{-16}	1.1870	65.38
3	464.0151	-1.35×10^{-7}	2.2950	65.38
4	9.7953	9.41×10^{-8}	8.1180	182.19
5	-	3.00×10^{-16}	4.1337	92.91
6	1699.3825	3.70×10^{-16}	0.1635	63.55
7	521.6618	3.40×10^{-16}	1.1116	58.69
8	29.1029	-5.22×10^{-8}	2.2977	65.38
9	39.5433	-7.71×10^{-8}	1.8017	112.41

Table 7 also shows that when mass increases, NLO response increases. This can be seen by comparing Structures 6 and 7 which have the same exact structures except different metals. The same case would also apply when comparing Structures 8 and 9 which have the same exact structures except different metals. From QSAR calculation, we can also obtain the models to see whether the compound possesses good NLO properties or not. From Table 8, QSAR models were successfully generated for each descriptor with separate calculations. Hence, when the metal mass is obtained and inserted into the QSAR model, it can be determined whether that particular compound possesses good NLO properties or not.

In this study, calculations for QSAR can only be carried out with one descriptor at a time due to insufficient metal complexes with n_2 value, but this study can be a preliminary study for future researches to strive. In the future, multiple effect calculation can be performed with enough geometrically optimized structures and experimental n_2 values.

Conclusion

In this study, by using Gaussian16 with SEM, it can be seen that Structure 7 has the highest optimization energy of 1.0288 a.u. and Structure 4 has the lowest optimization energy of 0.7133 a.u. Structure 2 has the highest dipole moment with 11.85 D while Structure 5 has the lowest dipole moment with 0.00 D. Structure 4 has the highest band gap energy of 8.1180 eV while Structure 6 has the lowest band gap

energy of 0.1635 eV. For β_{tot}, Structure 2 has the highest value while Structure 5 has no value because of the 0.00 D that could not generate dipole orientation to obtain β_{tot} value.

On QSAR part, it can be seen that out of the 4 descriptors studied, 2 parameters significantly affect NLO responses of metal complexes which are the effect of band gap energy with R Square of 0.445 and effect of metal mass with R Square of 0.308. The QSAR models that were obtained are y = 0.445x for effect of band gap and y = 0.308x for effect of metal mass.

For future research, it is highly recommended that a suitable method and basis set should be used for Gaussian calculations to obtain a more accurate set of data. Other than that, drawing of structures for the compounds studied should be symmetrical otherwise the calculations for dipole moment would not be accurate. The number of compounds that are used for QSAR should be high as well so that a better QSAR model could be obtained.

Acknowledgement

I would like to thank all people who have supported the research and sincere appreciation towards my final year project supervisor for the guidance, encouragement and advice.

References

[1] Stucky, G. D., Marder, S. R., & Sohn, J. E. (1991). Linear and Nonlinear Polarizability. *ACS Symposium Series*, 2.

[2] Maiman, T. H. (1960). Stimulated Optical Radiation in Ruby. *Nature*, *187*(4736), 493.

[3] Hagar, M., Soliman, S. M., Massoud, R. A., & Zaid, M. M. (2016). QSAR and DFT Studies on Non-Linear Optical Properties of Some Schiff Bases Derived from Salicylaldehyde and Nitroanilines. *Asian Journal of Chemistry*, *28*(2), 351.

[4] Cronin, M. T. D. (2009). Quantitative Structure–Activity Relationships (QSARs) – Applications and Methodology. *Challenges and Advances in Computational Chemistry and Physics*, 3.

[5] Liyanage, P. S., de Silva, R. M., & de Silva, K. (2003). Nonlinear optical (NLO) properties of novel organometallic complexes: high accuracy density functional theory (DFT) calculations. *Journal of Molecular Structure: THEOCHEM*, *639*(1–3), 195.