Calculation of Visible Absorption Maxima of Phthalocyanine Compounds by Quantum Theory

Shen Feng YUAN[1]*, Zhi Rong CHEN[1], Huai Xun CAI[2]

[1]Department of Chemical Engineering, Zhejiang University, Hangzhou 310027
[2]The R&D Center of Juhua Corp. LTD., Hangzhou 310018

Abstract: Based on HYPERCHEM, the structures of five phthalocyanie compounds were optimized with PM3 and their visible absorption maxima were calculated with ZINDO/S method by selecting appropriate π-π overlap weighting factor ($OWF_{\pi\text{-}\pi}$), the agreement with experiment was excellent. The relationship between $OWF_{\pi\text{-}\pi}$ and molecular structure parameters was obtained by the method of stepwise regression and was explained in terms of quantum theory.
$$OWF_{\pi\text{-}\pi}=0.58126+0.04562ANC1+0.03839X.$$
Where, ANC1 and X are the symbols of average net charges on coordinated bonded nitrogens and electronegativity of central atom, respectively.

Keywords: Phthalocyanine compounds, visible absorption maximum, ZINDO/S, stepwise regression.

Phthalocyanine compounds have attracted great interest of scientists for their important applications in the fields of colourants, optical data storage, anti-cancer agents, solar energy conversion and catalysts *etc*[1~4].   As colourants, one of the important properties is their visible absorption maxima, they had been predicted by quantum theory in many studies, but the agreement with experiment was not satisfactory[4~7].   In this study, the visible absorption maxima of five phthalocyanine compounds were calculated successfully with ZINDO/S method by selecting appropriate π-π overlap weighting factor ($OWF_{\pi\text{-}\pi}$).

Results and Discussion

Optimization of the structures

Former researches showed that the carbon and nitrogen alternated 16-numbered ring in phthalocyanine compounds had the largest extent of π-electron delocalization and the four benzene units were equivalent[7,8].   Based on these, the structures of five phthalocyanine compounds were optimized by PM3 program in this study.   Taking zinc phthalocyanine for example, the results were shown in **Figure 1** and **Table 1**.

As shown in **Table 1**, the four nitrogens bonded with zinc were not completely the

---

same.   For N2 and N10, their net charges were almost the same, but the length of the corresponding carbon-nitrogen bonds was different, however, for N6 and N14, it was in the opposite situation.   Accordingly, the four nitrogens could be classified as two sorts, those whose carbon-nitrogen bond length was different (could be considered as one single-bond and the other double-bond) could be thought to be bonded with zinc by coordinated bonds, and those whose carbon-nitrogen bond length was the same (could be considered as two single-bonds) could be thought to be bonded with zinc by covalent bonds.   This is in accordance with the treatment in typical structures of phthalocyanine compounds.   The optimized structures of phthalocyanine compounds in this study were similar to that of zinc phthalocyanine, the results were shown in **Table 2**.

Figure 1   Optimized structure of zinc phthalocyanine
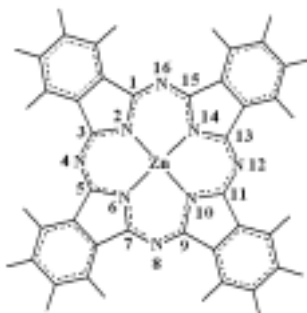
Table 1   Data of interest of bond length and net charges on nitrogens

bond length (Å)				net charges on nitrogens	
C1—N2	1.36558	C9—N10	1.44618	N2	0.105163
N2—C3	1.44618	N10—C11	1.36558	N6	0.207265
C5—N6	1.39646	C13—N14	1.41591	N10	0.105191
N6—C7	1.39648	N14—C15	1.41591	N14	-0.014779

Table 2   Average net charges on nitrogens and electronegativity of central atom

compounds	ANC[a]	ANC1[b]	ANC2[c]	X[d]
phthalocyaninefree base	0.00999	-0.24511	0.26509	0[e]
magnesium phthalocyanine	-0.04262	-0.06677	-0.01847	1.31[f]
zinc phthalocyanine	0.10071	0.10518	0.09624	1.65[f]
iron phthalocyanine	0.37307	0.41424	0.33190	1.83[f]
nickel phthalocyanine	0.53871	0.54775	0.52967	1.91[f]

[a]Average net charges on four nitrogens.   [b]Average net charges on coordinated bonded nitrogens. [c]Average net charges on covalent bonded nitrogens.   [d]Electronegativity of central atom.   [e]Set electronegativity as zero personally in absence of central atom.   [f]Data from HYPERCHEM.

Visible absorption maxima and relationship between OWF$_{\pi\text{-}\pi}$ *and structure parameters*

Based on the optimized structures above, their visible absorption maxima were calculated by ZINDO/S method.   The key was the selection of corresponding parameters, among which OWF$_{\pi\text{-}\pi}$ had primary influence on the calculated results. OWF$_{\pi\text{-}\pi}$ could be considered as the extent of π-electron delocalization, different compounds should have different values, but researches concerned with how to evaluate

$OWF_{\pi-\pi}$ and its influence on visible absorption maxima had not been seen in the literature.

In the calculation, the maximum excitation energy of configuration interaction was set as 10eV and the σ-σ overlap weighting factor was set as 1.267, $OWF_{\pi-\pi}$ was determined by comparison of calculated visible absorption maxima with those of observed. Besides the observed visible absorption maxima[9], the calculated results were also shown in **Table 3**.

Table 3   Observed visible absorption maxima and corresponding calculated results

No.	compounds	λ_{obs} (nm)[a]	calculated results with ZINDO/S method			λ (nm)
			$OWF_{\pi-\pi}$	λ_{cal} (nm)	$f^{[b]}$	
1	phthalocyanine free base	686	0.570	689.74	0.642	685.56
				681.91	0.735	
2	magnesium phthalocyanine	666	0.629	666.29	0.959	666.29
				655.18	0.931	
3	zinc phthalocyanine	661	0.649	664.97	1.069	661.26
				657.55	1.070	
4	iron phthalocyanine	676	0.670	676.09	0.853	676.09
				660.47	0.808	
5	nickel phthalocyanine	651	0.680	653.02	1.049	651.05
				649.08	1.059	

[a]Observed absorption maxima in vapor phase.   [b]Oscillator strength.

Seen from **Table 3**, each compound had two calculated visible absorption maxima. For compounds **1, 3** and **5**, the difference between the two calculated maxima was very small (<8 nm), in factual absorption spectroscopy, the two maxima overlap each other, a weighting average should be defined to represent the maximum of factual absorption spectroscopy as follows:

$$\lambda=(\lambda_1 f_1+\lambda_2 f_2)/(f_1+f_2) \qquad (1)$$

Where λ_1 and λ_2 were wavelengths of the two maxima and f_1, f_2, the corresponding oscillator strength. For compounds **2** and **4**, the difference between the two calculated maxima was somewhat too large (>11 nm), the maximum with lower strength had no influence on the factual absorption maximum, but appeared as a shoulder of that with higher strength, therefore, the maximum with higher strength should be used to represent the maximum of factual absorption spectroscopy.

In order to reveal the relationship between $OWF_{\pi-\pi}$ and structure parameters, the method of stepwise regression was used and the relationship obtained was shown in equation **(2)**. The validity of equation **(2)** was shown in **Figure 2** (R=0.99995) and **Table 4**. As shown, the agreement was excellent.

In terms of quantum theory, the extent of π-electron conjugation of the 16-numbered ring in phthalocyanine compounds was determined by the extent of delocalization of π-electrons in the ring, whose embodiment in phthalocyanine compounds was net charges on nitrogens, especially the nitrogens bonded with central atom, and in turn, the net charges on nitrogens were mainly determined by electronegativity of central atom. Moreover, considering the specificity of coordinated

bond, the net charges on coordinated bonded nitrogens should also affect the extent of π-electron conjugation. In summary, the deciding factor of $OWF_{\pi-\pi}$ should be electronegativity of central atom, and the net charges on coordinated bonded nitrogens should be a secondary factor. The results of regression (equation (**2**) and **Table 4**) were in accordance with the reasoning above very well.

$$OWF_{\pi-\pi}=0.58126+0.04562ANC1+0.03839X \qquad (2)$$

Figure 2   Relationship between $OWF_{\pi-\pi}$ calculated
by equation (**2**) and that used in **Table 3**
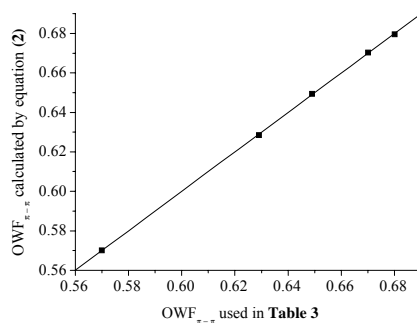
Table 4   Multiple linear regression results using ORIGIN

parameter	value	Error	t-value	prob>|t|
intercept	0.58126	8.36344E-4	695.00431	<0.0001
ANC1	0.04562	0.00179	25.49554	0.00153
X	0.03839	7.51193E-4	51.1088	3.82613E-4

The significance of this study lied in that for a given phthalocyanine compound, the visible absorption maximum could be predicted successfully. This was important in improving the accuracy of visible absorption spectroscopy prediction and revealing the relationship between visible absorption spectroscopy and molecular structure, and in some sense, it also helped in molecular structure design of phthalocyanine dyes and pigments. Further study is in progress.

References

1.   B. N. Achar, P. K. Jayasree, *Synthetic Metals*, **1999**, *104*, 101.
2.   B. X. Peng, D. T. Gao, T. T. Yan, *Zhongguo Kexueyuan Yanjiushengyuan Xuebao (J. Graduate School, Academia Sinica,* Chinese), **2000**, *17*(1), 43.
3.   B. N. Achar, P. K. Jayasree, *Synthetic Metals*, **2000**, *114*,219.
4.   X. D. Gong, H. M. Xiao, H. Tian, *J. Mol. Struct., (Theochem)*, **2002**, *593*, 93.
5.   R. M. Christie, *Dyes Pig*m., **1995**, *27*(1), 35.
6.   L. A. Soares II, M. Trsic, B. Berno, *et al.*, *Spectrochim. Acta, Part A*, **1996**, *52*, 1245.
7.   J. Mack, M. J. Stillman, *Coord. Chem. Rev.*, **2001**, *219-221*, 993.
8.   V. Mastryukov, C. Y. Ruan, M. Fink, *et al.*, *J. Mol. Struct.*, **2000**, *556*, 225.
9.   L. Edwards, M. Gouterman, *J. Mol. Spectrosc.*, **1970**, *33*, 292.