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Study on the Prediction of Visible Absorption Maximum of Phthalocyanine Compounds by Semiempirical Quantum Methods

S. Feng Yuan* and Z. Rong Chen

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, Peoples Republic of China

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To improve the prediction accuracy of visible absorption maximum, a new idea is introduced in this article, that is, $\mathrm{OWF}_{\pi-\pi}$ ($\pi-\pi$ overlap weighting factor, one of the adjustable parameters in ZINDO/S method) is considered as a measurement of the extent of π-electron delocalization, rather than a certain fixed value applicable to all molecules. The results of this study show that the new idea is feasible in improving the prediction accuracy and there is some relationship between $\mathrm{OWF}_{\pi-\pi}$ and molecular structural parameters for phthalocyanine compounds. The relationship could be extrapolated to compounds of the same series. From the point of view of electron transition, the electron transition from regions around one covalent bonded nitrogen to those around the other covalent bonded nitrogen and the two coordinate bonded nitrogens, i.e., the transition from HOMO to LUMO and LUMO+1, results in the visible absorption maximum of phthalocyanine compounds.

1. Introduction

Phthalocyanine compounds have attracted great interest of scientists for their important applications in the fields of colorants, optical data storage, anticancer agents, solar energy conversion and catalysts, etc.[1−4] As colorants, one of their most important properties is their visible absorption maximum; it has been predicted by quantum theory in many studies, but the agreement with experiment is not satisfactory.[4−7] A new idea is introduced in this article to improve the prediction accuracy of visible absorption maximum.

Developed by the research group of Michael C. Zerner of the Quantum Theory Project at the University of Florida, the so-called ZINDO/S[8] is a modified INDO (intermediate neglect of differential overlap) method parametrized to reproduce UV/visible spectral transition. A new pair of adjustable parameters was introduced to ZINDO/S by its developers, i.e., $\sigma-\sigma$ overlap weighting factor (simplified as $\mathrm{OWF}_{\sigma-\sigma}$) and $\pi-\pi$ overlap weighting factor (simplified as $\mathrm{OWF}_{\pi-\pi}$), to modify the resonance integrals for the off-diagonal elements of the Fock matrix. Adjusting the parameters provides a mechanism to adjust the relative contributions of σ vs π bonding. Therefore, the value of $\mathrm{OWF}_{\pi-\pi}$ could be considered as a measurement of the extent of π-electron delocalization.

Since almost all UV/visible absorption originate from electron transition involving π-electron or π-orbital, the extent of π-electron delocalization has great influence upon its UV/visible absorption spectrum; that is to say, different UV/visible absorption spectra would be obtained with different values of $\mathrm{OWF}_{\pi-\pi}$. Therefore, the value of $\mathrm{OWF}_{\pi-\pi}$ used in the calculation is of great importance.

In HyperChem 7 (the software used in the paper), the default value is 1.267 and 0.585 for $\mathrm{OWF}_{\sigma-\sigma}$ and $\mathrm{OWF}_{\pi-\pi}$ respectively, however, considering the variety of molecular structure and the complexity of molecular conformation, the extent of π-electron delocalization is different for different molecules. In other words, different values of $\mathrm{OWF}_{\pi-\pi}$ should be used for different molecules. Although several different values for $\mathrm{OWF}_{\pi-\pi}$ have been used in the literature,[9] researches concerned how to evaluate $\mathrm{OWF}_{\pi-\pi}$ and its influence on UV/visible absorption spectrum have not been seen. In this study, the relationship between $\mathrm{OWF}_{\pi-\pi}$ and molecular structural parameters is obtained for phthalocyanine compounds and using the relationship obtained, the prediction accuracy is improved greatly for compounds of the same series.

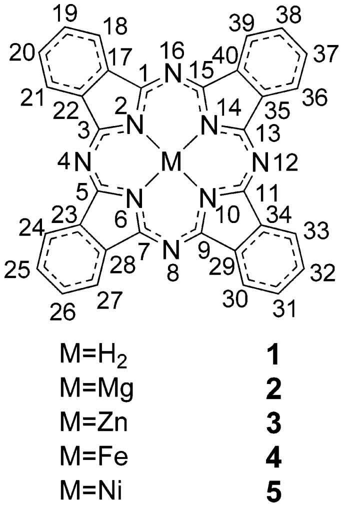

Figure 1. Molecular structure and numbering of compounds **1**−**5**.

2. Calculation Method

2.1. Geometry Optimization. The PM3[10,11] method is based on the neglect of the diatomic differential overlap (NDDO) approximation, and satisfactory results could be obtained in the geometry optimization of phthalocyanine.[12] In this article, the geometry of phthalocyanine compounds is also optimized by PM3 method.

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.[7,13] In this paper, the 16-numbered ring and the four benzene units are all set as aromatic bonds (broken lines in Figure 1). On the basis of the structure

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* To whom correspondence should be addressed. E-mail: ysf@zju.edu.cn

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TABLE 1: Data of Interest of Bond Length and PM3 Net Charge of Compound 3

bond length/Å				PM3 net charge	
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

constructed above, the “Model Build” conformation is used as the initial one for geometry optimization. In the PM3 method, RHF is used, and in SCF controls, the accelerate convergence is selected and the convergence limit is set as 0.01; in optimization calculation, the algorithm of Polak−Ribiere (conjugated gradient) is adopted, and as termination condition, the RMS gradient is set as 0.01.

2.2. Visible Absorption Maximum. Using the optimized geometry, the visible absorption maximum is calculated by the ZINDO/S method and the PM3 method.

In calculation, RHF is used and in SCF controls, the accelerate convergence is selected and the convergence limit is set as 0.01; to save computing time, the maximum excitation energy of singlet excited configuration interaction is set as 10 eV. In addition, for the ZINDO/S method, $\mathrm{OWF}_{\sigma-\sigma}$ is set as 1.267 (default value), whereas $\mathrm{OWF}_{\pi-\pi}$ is so evaluated so that the calculated visible absorption maximum could coincide with that of the observed. All calculations were performed on a Pentium 4 computer.

3. Results and Discussion

3.1. Geometry Optimization. The molecular structure and numbering of compounds **1**−**5** are shown in Figure 1. For the optimized geometry of compound **3**, as an example, partial results of bond length and PM3 net charge are listed in Table 1. As shown, the four nitrogens bonded with central atom M (here it is zinc) are not completely the same. For N2 and N10, their net charge is almost the same, but the length of the corresponding carbon−nitrogen bonds is different. However, for N6 and N14, it is the opposite situation. The optimized geometries of other compounds in this study are all similar to that of compound **3**. Accordingly, the four nitrogens could be classified as two sorts, those whose carbon−nitrogen bond length is different (could be considered as one single bond and the other as double bond) should be thought to bond with central atom by coordinate bonds, whereas those whose carbon−nitrogen bond lengths are the same (could be considered as two single bonds) should be thought to bond with the central atom by covalent bonds. This is in accordance with the treatment of typical structures of phthalocyanine compounds.[1]

On the basis of the optimized geometry of compounds **1**−**5**, the PM3 average net charge on nitrogens is presented in Table 2, along with the electronegativity value of the central atom.

3.2. Visible Absorption Maximum. In comparison with the observed visible absorption maximum,[14] the appropriate $\mathrm{OWF}_{\pi-\pi}$ value should be used in the ZINDO/S method, and the corresponding calculated results are shown in Table 3. The electron transition and orbital composing corresponding to the electron transition are listed in Tables 4 and 5. To illustrate the necessity of varing $\mathrm{OWF}_{\pi-\pi}$ in the ZINDO/S method, Table 6 presents the calculated results based on the PM3 method and the default ZINDO/S method ($\mathrm{OWF}_{\pi-\pi}$ is set as 0.585).

Seen from Table 3, each compound has two calculated visible absorption maxima. For compounds **1**, **3**, and **5**, the difference between the two calculated maxima is so small (<8 nm) that the two maxima overlap each other, so a weighting average should be defined to reflect the absorption maximum as follows:

TABLE 2: Average Net Charge on Nitrogens and Electronegativity Value of Central Atom

compound	ANC[a]	ANC1[b]	ANC2[c]	X[d]
1	0.00999	−0.24511	0.26509	0[e]
2	−0.04262	−0.06677	−0.01847	1.31
3	0.10071	0.10518	0.09624	1.65
4	0.37307	0.41424	0.33190	1.83
5	0.53871	0.54775	0.52967	1.91

[a] Average net charge on nitrogens bonded with central atom (here N2, N6, N10 and N14). [b] Average net charge on coordinate bonded nitrogens (here N2 and N10). [c] Average net charge on covalent bonded nitrogens (here N6 and N14). [d] Electronegativity value of central atom got from HyperChem 7. [e] Electronegativity value is set as zero personally in absence of central atom.

TABLE 3: Observed Visible Absorption Maximum and Corresponding Calculated Results

		calculated results			
compound	λ_{obs} [a]/nm	$\mathrm{OWF}_{\pi-\pi}$	λ_{cal} [b]/nm	f[c]	λ[d]/nm
1	686	0.570	689.74	0.642	685.56
			681.91	0.735	
2	666	0.629	666.29	0.959	666.29
			655.18	0.931	
3	661	0.649	664.97	1.069	661.26
			657.55	1.070	
4	676	0.670	676.09	0.853	676.09
			660.47	0.808	
5	651	0.680	653.02	1.049	651.05
			649.08	1.059	

[a] Observed visible absorption maximum in vapor phase. [b] Only those in visible region with higher f value are given. [c] Oscillator strength. [d] Representative wavelength reflecting the absorption maximum.

TABLE 4: Electron Transition Corresponding to the Calculated Absorption Maximum

compound	λ_{cal}/nm	electron transition
1	689.74	HOMO → LUMO
	681.91	HOMO → LUMO+1
2	666.29	HOMO → LUMO
		HOMO → LUMO+1
	655.18	HOMO → LUMO
		HOMO → LUMO+1
3	664.97	HOMO → LUMO+1
	657.55	HOMO → LUMO
4	676.09	HOMO → LUMO
	660.47	HOMO → LUMO+1
5	653.02	HOMO → LUMO+1
	649.08	HOMO → LUMO

$$\lambda = (\lambda_1 f_1 + \lambda_2 f_2)/(f_1 + f_2) \tag{1}$$

where λ_1 and λ_2 are wavelengths of the two maxima and f_1 and f_2, the corresponding oscillator strengths. For compounds **2** and **4**, the difference between the two calculated maxima is somewhat too large (>11 nm), the maximum with lower strength appears as a shoulder of that with higher strength; therefore, the maximum with higher strength should be used to reflect the absorption maximum.

It is indicated in Table 4 that consistent with the known facts of dye absorption in most cases, the electron transition corresponding to the calculated absorption maximum is from HOMO to LUMO or/and from HOMO to LUMO+1. The data in Table 5 indicated that HOMO consists mainly of carbon atoms around N14, one of the covalent bonded nitrogens, LUMO consists mainly of carbon atoms around N6, the other covalent bonded nitrogens, and LUMO+1 consists mainly of carbon atoms around N2 and N10, the coordinate bonded nitrogens. Therefore, the electron transition from regions around one covalent bonded nitrogen to those around the other covalent bonded nitrogen

TABLE 5: Contribution of Component Atoms to the Given Molecular Orbitals[a]

	compound **1**			compound **2**			compound **3**			compound **4**			compound **5**		
orbital	HOMO	LUMO	LUMO+1	HOMO	LUMO	LUMO+1	HOMO	LUMO	LUMO+1	HOMO	LUMO	LUMO+1	HOMO	LUMO	LUMO+1
C1	8.80		8.30	11.66		7.73	10.31		8.34	10.01		7.87	10.27		8.50
N2		4.31			4.88			4.56			5.53			4.78	
C3	3.52	3.49	9.47	6.19	4.42	9.61	6.36	4.55	10.30	6.36	3.57	9.63	7.02	3.73	9.88
N4		6.54			5.39			3.53	1.87		3.41	2.00		3.53	2.26
C5	1.87	14.25	4.24	3.39	12.31	2.12	4.41	12.42	2.23	5.01	11.42	2.32	5.39	11.48	2.15
N6			2.37			3.74			4.01			5.03			4.43
C7	1.87	14.24	4.24	3.00	15.06		4.41	12.42	2.22	5.03	11.53	2.32	5.39	11.53	2.11
N8		6.53				3.73		3.53	1.88		3.45	1.99		3.51	2.28
C9	3.52	3.49	9.47	3.63	6.48	9.76	6.36	4.55	10.29	6.40	3.61	9.63	7.01	3.78	9.84
N10		4.31			3.45			4.57			5.54			4.79	
C11	8.80		8.30	8.79		9.05	10.31		8.34	10.05		7.83	10.26		8.52
N12		2.56	4.29		2.70	4.33		2.93	4.79		2.93	4.14		3.00	4.34
C13	19.93	2.18	3.24	15.92	4.19	3.35	14.92	5.83	2.16	14.58	5.59	2.19	13.37	6.60	2.14
N14			3.16			3.92			4.34			4.53			4.67
C15	19.93	2.18	3.24	17.92	4.19	1.78	14.92	5.83	2.15	14.54	5.48	2.23	13.38	6.62	2.10
N16		2.56	4.29		3.30	4.98		2.92	4.79		2.92	4.11		2.98	4.37
C17			3.04			3.48			3.71			3.68			3.55
C18				1.97			1.71			1.52			1.75		
C19			2.15			2.31			2.51			2.42			2.32
C20			1.76			1.82			1.96			1.92			1.97
C21															
C22			2.61			2.87			3.10			3.19			3.12
C23		6.55			4.60			4.18			4.54			4.01	
C24		1.80	1.69												
C25		4.47			3.42			2.91			2.91			2.70	
C26		4.47			2.85			2.91			2.89			2.69	
C27		1.80	1.69		1.81										
C28		6.55			4.18			4.18			4.53			4.00	
C29			2.61			3.60			3.10			3.18			3.13
C30															
C31			1.76			2.38			1.96			1.92			1.98
C32			2.15			2.79			2.51			2.42			2.31
C33							1.71			1.53			1.75		
C34			3.04			4.09			3.71			3.68			3.54
C35	2.85			2.22	1.99		1.56	2.38		1.84	2.57			2.54	
C36	4.23			3.08			2.78			2.48			2.42		
C37	3.42			2.75			2.09			2.00			1.78	1.52	
C38	3.42			2.29			2.09			2.00			1.78	1.52	
C39	4.23			3.50			2.78			2.47			2.42		
C40	2.85			1.72	2.05		1.56	2.38		1.84	2.59			2.53	

[a] The value is in percent, and for the sake of simplicity, values less than 1.5 have been excluded.

TABLE 6: Calculated Results Based on PM3 and Default ZINDO/S Method

	PM3		ZINDO/S	
compound	λ_{cal} [a]/nm	f[b]	λ_{cal} [a]/nm	f[b]
1	569.27	0.357	675.52	0.665
	420.60	0.726	668.80	0.758
2	628.57	0.350	705.21	0.889
	509.54	0.414	694.61	0.863
3	641.07	0.380	722.40	0.978
	535.45	0.534	714.12	0.969
4	651.39	0.173	828.56	0.566
	610.50	0.178	745.60	0.703
5	609.60	0.297	734.85	0.916
	545.45	0.382	730.30	0.909

[a] Only those in visible region with higher f value are given. [b] Oscillator strength.

and the two coordinate bonded nitrogens, i.e., the transition from HOMO to LUMO and LUMO+1, results in the visible absorption maximum of phthalocyanine compounds.

Seen from Table 6, the calculated results based on PM3 and the default ZINDO/S method deviate far from observed values, and there is no relationship between calculated results and observed ones. Therefore, the calculation of the visible absorption maximum using the ZINDO/S method with an unfixed $\text{OWF}_{\pi-\pi}$ value is an effective way to improve prediction accuracy.

3.3. Relationship between $\text{OWF}_{\pi-\pi}$ and Molecular Structural Parameters. To reveal the relationship between $\text{OWF}_{\pi-\pi}$ and molecular structural parameters, average net charges on nitrogens and the electronegativity value of central atom (ANC, ANC1, ANC2, and X in Table 2) are used to correlate with the value of $\text{OWF}_{\pi-\pi}$ in Table 3. Using the method of stepwise multiple linear regression, the results are given in eq 2 and Table 7. The validity of eq 2 is shown in Figure 2 ($R = 0.99995$).

$$\text{OWF}_{\pi-\pi} = 0.58126 + 0.04562\text{ANC1} + 0.03839X \quad (2)$$

TABLE 7: Results of Multiple Linear Regression

parameter	value	error	t	prob > $\|t\|$
intercept	0.58126	8.36E-4	695.0	<1E-4
C_1 [a]	0.04562	1.79E-3	25.5	1.53E-3
C_2 [b]	0.03839	7.51E-4	51.1	3.83E-4

[a] The coefficient of ANC1. [b] The coefficient of X.

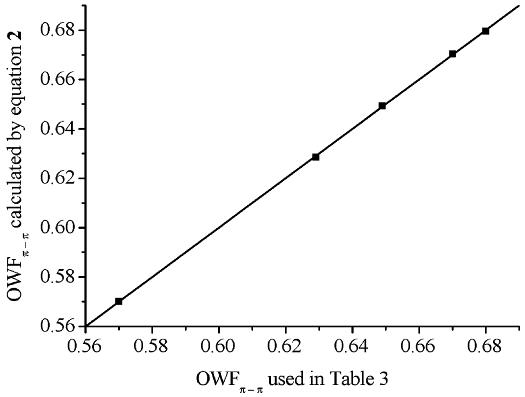

Figure 2. Relationship between $\text{OWF}_{\pi-\pi}$ calculated by eq 2 and that used in Table 3.

TABLE 8: Calculated Results and Observed Visible Absorption Maximum for Phthalocyanine Derivatives

substituent[a]	M	ANC1	$OWF_{\pi-\pi}$ [b]	λ_{cal} [c]/nm	λ[d]/nm	λ_{obs} [e]/nm	$\lvert\lambda - \lambda_{\mathrm{obs}}\rvert$	ref
19,25,31,37-tetra-*tert*-butyl	H_2	−0.24663	0.570	692.66 (0.637) 684.27 (0.730)	688.18	696[f]	7.82	5
19,25,31,37-tetraphenyl	H_2	−0.24653	0.570	708.78 (0.784) 700.56 (0.798)	704.63	713[g]	8.37	5
19,25,31,37-tetranitro	H_2	−0.23874	0.570	724.67 (0.743) 700.57 (0.728)	724.67	720[f]	4.67	5
19,25,31,37-tetramethoxy	H_2	−0.24870	0.570	696.64 (0.656) 690.14 (0.730)	693.22	702[g]	8.78	5
19,25,31,37-tetraphenoxy	H_2	−0.24696	0.570	701.74 (0.664) 690.53 (0.751)	690.53	701[g]	10.47	5
18,21,24,27,30,33,36,39-octa-ethoxy	H_2	−0.25354	0.570	720.09 (0.663) 700.56 (0.554)	720.09	724[h]	3.91	2
19,25,31,37-tetraphenoxy	Mg	−0.06604	0.628	676.65 (0.973) 663.52 (0.921)	676.65	682.1[i]	5.45	18
19,25,31,37-tetra-*tert*-butyl	Zn	0.10409	0.649	669.32 (1.068) 662.12 (1.070)	665.72	678[j]	12.28	5
19,25,31,37-tetraphenyl	Zn	0.10391	0.649	688.50 (1.171) 681.86 (1.181)	685.16	694[k]	8.84	5
18,24,30,36-tetranitro	Zn	0.11038	0.650	663.10 (1.072) 654.77 (1.070)	658.94	671[i]	12.06	16
19,25,31,37-tetramethoxy	Zn	0.10453	0.649	669.16 (1.063) 665.78 (1.064)	667.47	680[g]	12.53	5
19,25,31,37-tetraphenoxy	Zn	0.10497	0.649	673.74 (1.085) 668.32 (1.090)	671.02	679.5[i]	8.48	18
18,24,30,36-tetra[3′,5′-bis-(trifluoromethyl)]phenoxy	Zn	0.10563	0.649	676.88 (1.087) 670.11 (1.084)	673.50	687[l]	13.50	2
19,25,31,37-tetracarboxy	Zn	0.10548	0.649	678.38 (1.129) 668.05 (1.123)	678.38	673[m]	5.38	17
19,25,31,37-tetraphenyl	Ni	0.54868	0.680	678.07 (1.171) 674.53 (1.171)	676.30	683[k]	6.70	5
19,25,31,37-tetranitro	Ni	0.56085	0.680	679.99 (1.123) 675.22 (1.124)	677.60	691[f]	13.40	5
19,25,31,37-tetra(3′-trifluoromethyl)phenoxy	Ni	0.54678	0.680	660.93 (1.052) 654.86 (1.047)	657.90	667[n]	9.10	15
19,25,31,37-tetra(3′-methyl)phenoxy	Ni	0.54340	0.679	662.35 (1.056) 655.86 (1.063)	659.09	669[n]	9.91	15

[a] The numbering is the same as that given in Figure 1. [b] Calculated based on eq 2. [c] Calculated results with ZINDO/S method; the value in parentheses is the corresponding oscillator strength. [d] Representative wavelength reflecting the absorption maximum, when the difference between the two calculated wavelength is less than 10 nm, a weighting average according to eq 1 is adopted, otherwise, the one with higher strength is adopted. [e] Observed visible absorption maximum in given solvent as indicated below. [f] 1-Chloronaphthalene. [g] 1,2,4-Trichlorobenzene. [h] Toluene. [i] *N*,*N*-Dimethylformamide. [j] Benzene. [k] Nitrobenzene. [l] Chloroform. [m] Ethanol. [n] Tetrahydrofuran.

To illustrate the validity of eq 2 further, 18 phthalocyanine derivatives were studied and the results are presented in Table 8. As indicated, the difference between calculated maximum and observed value is less than 14 nm. Considering solvent effect, this is a good agreement.

4. Conclusion

The results of this study show that the idea of varing $OWF_{\pi-\pi}$ in UV/visible spectrum calculation is feasible in improving prediction accuracy and that there is indeed some relationship between $OWF_{\pi-\pi}$ and molecular structural parameters. The relationship could be extrapolated to compounds of the same series. From the point of view of electron transition, the electron transition from regions around one covalent bonded nitrogen to those around the other covalent bonded nitrogen and the two coordinate bonded nitrogens, i.e., the transition from HOMO to LUMO and LUMO+1, results in the visible absorption maximum of phthalocyanine compounds.

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

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