Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 77 (2008) 277–280

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Molecular structure and visible absorption maximum of cobalt phthalocyanine: Quantum calculations via semi-empirical methods

Fang Li [b,c], Qiguang Zheng [a,b,c,*], Guang Yang [a,b,c], Peixiang Lu [a,b,c]

[a] *State Key Laboratory of Laser Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, Hubei 430074, PR China*
[b] *Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, Hubei 430074, PR China*
[c] *School of Optoelectronics Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China*

Received 18 November 2006; received in revised form 16 May 2007; accepted 17 May 2007
Available online 2 June 2007

Abstract

The geometrical molecular structure of cobalt phthalocyanine was first optimized using the semi-empirical PM3 method and the electronic spectrum was then calculated using the ZINDO/S method. The results showed that the visible absorption maximum of cobalt phthalocyanine was precisely predicted by setting the $\pi-\pi$ overlap weighting factor parameter in the ZINDO/S method at 0.793. Furthermore, the study of molecular orbitals indicates that the visible absorption maximum corresponds to electronic transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The splitting of the visible absorption maximum is related to the splitting of the doubly degenerated e_g molecular orbital.

Keywords: Cobalt phthalocyanine; Molecular structure; Visible absorption maximum; PM3; ZINDO/S

1. Introduction

Phthalocyanines enjoy widespread use as pigments because of their brilliance and beauty [1]. They possess outstanding stability to light, heat, acids and alkalis; more recently, they have been used as organic semiconductors for gas sensors, infrared dyes for laser technology, anti-cancer agents, in optical data storage and as low-dimensional conducting materials [2–15]. Cobalt phthalocyanine (CoPc) and its derivatives are effective catalysts for the oxidation of sulfur-containing substrates [16] and are effective in the catalytic oxidation of mercaptans in oil fractions and in removing alkali sulfides from industrial waste water [17,18]; they can also serve as active elements in chemical sensors, especially for the detection of NO_2 [19,20].

To date, most of the research has been focused on the synthesis of cobalt phthalocyanine derivatives and their electrochemical properties [9,21,22] whilst, in contrast, studies of the spectral properties of CoPc are rare. Since it is very important to understand how their visible absorption spectrum is related to molecular structure, in this present paper, a quantum chemistry calculation of CoPc has been carried out to elucidate the structure–spectrum relationship. The geometrical molecular structure of CoPc was first optimized using the PM3 method and the electronic spectrum of CoPc was calculated using the ZINDO/S method. The visible absorption maximum was precisely calculated and well elucidated from the perspective of electronic transition.

2. Computational details

All semi-empirical quantum-chemical computations were performed using the HyperChem 7.0 computer program. Firstly, a dehydrophthalocyanine molecule, which has an

---

* Corresponding author. Tel./fax: +86 27 87543755.
E-mail address: qgzheng@mail.hust.edu.cn (Q. Zheng).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.05.009

entire conjugated system, was drawn. Then a Co atom was added to the center of the macro-ring of the dehydrophthalocyanine molecule with four unknown bonds connected to four nitrogen atoms in the isoindole rings. After constructing the skeleton of CoPc, the ‘‘Model Build’’ conformation was used as the initial model for geometry optimization. The geometry was then further optimized using the PM3 method, utilizing the Restricted Hartree Fock theory (RHF) and the self-consistent field (SCF) mode (which accounts for electron repulsion energies in solutions of the Schrodinger equation), with acceleration convergence selected and using a convergence limit of 0.01. In the optimization calculation, the algorithm of Polak–Ribiere (conjugated gradient) was adopted and, as termination condition, the RMS (Root Mean Square) gradient was set to 0.01.

Based on the optimized geometrical structure, the electronic spectrum was calculated using the ZINDO/S method. In this calculation, RHF was used and in the SCF mode, the acceleration convergence was selected and a convergence limit was set to 0.01; the maximum excitation energy of the excited singlet configuration interaction was adjusted to 10 eV. For the ZINDO/S method, the $\mathrm{OWF}_{\sigma-\sigma}$ ($\sigma-\sigma$ overlap weighting factor) was set to 1.267 as the default value; an appropriate value of $\mathrm{OWF}_{\pi-\pi}$ ($\pi-\pi$ overlap weighting factor) needs to be sought so that the calculated visible absorption maximum could coincide with that of observed.

3. Results and discussion

3.1. Molecular structure

The molecular structure and atomic numbering of CoPc are shown in Fig. 1. CoPc consists of a 16-membered inner ring of alternating carbon and nitrogen atoms, with a Co atom in the center and four outer benzene units. The bond lengths and bond angles are listed in Tables 1 and 2 along with the experimental values [23]. As shown in Tables 1 and 2, the calculated bond lengths and bond angles are in good agreement with the experimental values.

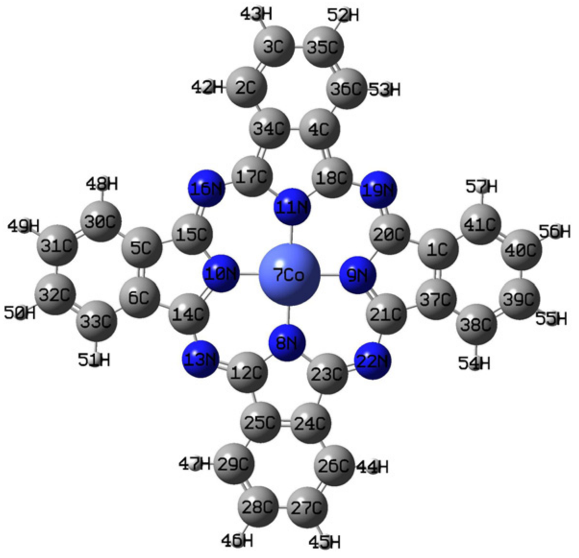

Fig. 1. The structure of cobalt phthalocyanine.

Table 1
Comparison of the calculated and experimental bond lengths/Å

Bond	Calculated value	Experimental value [23]
Co7–N9	1.934	1.919
N9–C21	1.392	1.380
C20–C19	1.325	1.235
C20–C1	1.465	1.457
C1–C37	1.416	1.398
C1–C41	1.383	1.397
C41–C40	1.400	1.396
C41–C39	1.390	1.410
C39–H55	1.095	0.960
C40–H56	1.095	0.980

The cobalt atom has a d^7 configuration. The calculations of Rosa and Baerends [24] showed that the half-filled CoPc d_z^2 orbital lies very close to the ligand HOMO (highest occupied molecular orbital). Fig. 2 depicts the contrasting situation in the case of CoPc in which the occupied (heavy lines) and unoccupied levels lie close to the Fermi energy as determined by the UHF-XR calculation of Reynolds and Figgis [25]. We can see clearly from the open-shell calculation that there should be considerable d-orbital participation in both the HOMO and LUMO (the lowest occupied molecular orbital), making CoPc an excellent candidate for observing direct d-orbital charge density [26].

The calculated Mulliken atomic charges of CoPc are listed in Table 3. The effective charge on cobalt atom is −0.275355, indicating that the bonding between Co atom and Pc is not purely ionic but significantly covalent. The high electronegativity of nitrogen leads to some local accumulation of charge. N8 and N11 are more negatively charged than N9 and N10, probably owing to the overlap of the former with the metal orbitals. Accordingly, the four nitrogen atoms can be classified into two groups. For one group, the carbon–nitrogen bond lengths are different, which can be considered as one single

Table 2
Comparison of the calculated and experimental bond angles

Angle/°	Calculated value	Experimental value [23]
N9Co7N8	90.01	90.00
Co7N9C20	126.48	126.50
C20N19C18	121.16	121.07
C21N9C20	105.64	107.00
N19C18N11	127.29	127.93
N19C20C1	123.65	121.93
N9C20C1	109.31	110.14
C20C1C41	132.04	132.06
C20C1C37	106.86	106.36
C1C37C38	121.00	121.58
C1C41C40	117.70	117.06
C41C40C39	121.23	121.36
C1C41H57	121.09	121.70
C41C40H56	119.17	119.90
C39C40H56	119.60	118.80

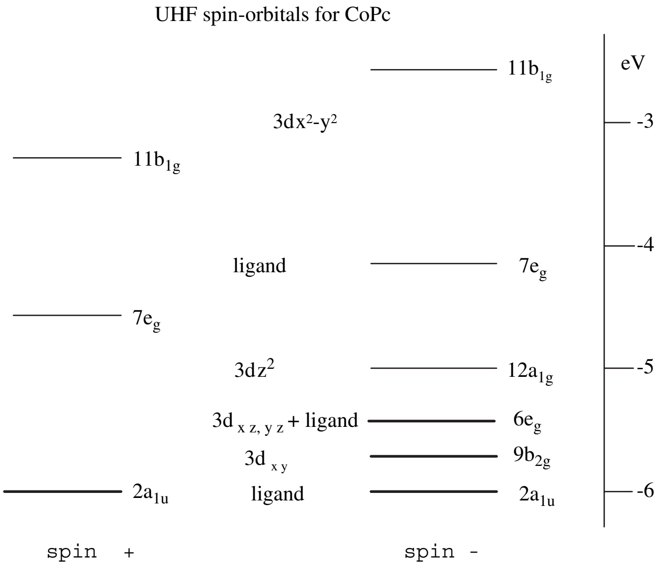

Fig. 2. Spin-orbital energies of cobalt(II) phthalocyanine near the Fermi energy. Heavy lines depict occupied levels while the thinner ones represent virtual (empty) orbitals. This diagram is based on data taken from Ref. [25].

bond and one double bond. These nitrogen atoms are connected to the central Co by coordinate bonds. Whereas, for the other group, the carbon–nitrogen bond lengths are the same, which can be considered as two single bonds. These nitrogen atoms are connected to the central Co by covalent bonds. This is in accordance with the treatment of typical structures of metal phthalocyanines [6].

3.2. Electronic absorption spectrum

Since almost all UV/visible absorption originates from electronic transitions involving π-electrons or π-orbitals, the extent of π-electron delocalization has a great influence upon its UV/visible absorption spectrum. This means that different UV/visible absorption spectra can be obtained with different values of $OWF_{\pi-\pi}$, which are considered as a parameter of the degree of π-electron delocalization in HyperChem [27]. Therefore, the value of $OWF_{\pi-\pi}$ used in the calculation is of great importance. In HyperChem, the default values are 1.267 and 0.585 for $OWF_{\sigma-\sigma}$ and $OWF_{\pi-\pi}$, respectively. However, considering the variety of molecular structure and the complexity of molecular conformation, the degree of π-electron delocalization is different for different molecules. In other words, different values of $OWF_{\pi-\pi}$ should be used for different molecules.

Thus, in order to predict the visible absorption maximum of CoPc, an appropriate $OWF_{\pi-\pi}$ value used in the ZINDO/S method needs to be sought. The results of the corresponding calculation are listed in Table 4. The 16-numbered ring of alternating carbon and nitrogen with the four benzene units in the structure of CoPc has the largest extent of π-electron delocalization. The π* molecular orbital is formed due to the unsaturation of four benzene units. Accordingly, the visible absorption maximum originates from the electronic transition from the π molecular orbital to the π* molecular orbital. It can be seen from Table 4 that the visible absorption maximum of CoPc splits into two peaks, λ_1 and λ_2. It results from the splitting of the doubly degenerated molecular orbital e_g (LUMO). In detail, the molecular orbital e_g splits into two orbitals e_g^H and e_g^L. The energy of e_g^H is higher than that of e_g. The energy of e_g^L is lower than that of e_g. Accordingly, the absorption maximum λ_1 originates from the electronic transition from a_{1u} (HOMO) to e_g^L, the absorption maximum λ_2 originates from the electronic transition from a_{1u} to e_g^H.

Table 4 shows that the difference between the two calculated maxima is so small that they overlap, so a weighting average should be defined to reflect the absorption maximum as follows [28].

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

where λ_1 and λ_2 are wavelengths of the two maxima, f_1 and f_2 are the corresponding oscillator strengths. The calculated absorption maximum of 656.85 nm is well consistent with the experimental result of 657 nm [29] when $OWF_{\pi-\pi} = 0.793$.

Table 3
Mulliken charge distributions of CoPc molecule

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C1	0.010316	C2	0.004715	C3	−0.011506	C4	0.010957
C5	0.010948	C6	0.010277	Co7	−0.275355	N8	−0.215531
N9	−0.215510	N10	−0.215516	N11	−0.215500	C12	0.279691
N13	−0.365426	C14	0.280399	C15	0.279607	C16	−0.365445
C17	0.280359	C18	0.279552	N19	−0.365387	C20	0.280279
C21	0.279752	N22	−0.36548	C23	0.280461	C24	0.010274
C25	0.010930	C26	0.004747	C27	−0.011487	C28	−0.010767
C29	0.003865	C30	0.003838	C31	−0.010792	C32	−0.011494
C33	0.004716	C34	0.010289	C35	−0.010800	C36	0.003851
C37	0.010913	C38	0.003894	C39	−0.010784	C40	−0.011461
C41	0.004698	H42	0.025087	H43	0.015921	H44	0.025087
H45	0.015927	H46	0.015910	H47	0.025306	H48	0.025322
H49	0.015931	H50	0.015902	H51	0.025103	H52	0.015917
H53	0.025297	H54	0.025301	H55	0.015898	H56	0.015918
H57	0.025093						

Table 4
Values of $OWF_{\pi-\pi}$ and corresponding calculated results

$OWF_{\pi-\pi}$	λ_1[a]/nm	f_1[b]	λ_2[a]/nm	f_2[b]	λ_{max}[c]
0.620	757.68	0.220	749.10	0.193	753.67
0.720	707.13	0.290	703.60	0.280	705.40
0.785	661.41	0.331	661.30	0.332	661.35
0.790	658.30	0.335	658.20	0.335	658.23
0.792	657.30	0.337	657.20	0.337	657.25
0.793	656.90	0.338	656.80	0.338	656.85
0.795	655.80	0.339	655.70	0.340	655.70
0.800	652.78	0.343	652.50	0.254	652.66
0.810	647.88	0.353	645.90	0.347	651.36
0.820	642.14	0.359	640.80	0.359	641.47

[a] Only those in the visible region with higher *f* values are given.
[b] Oscillator strength.
[c] Representative wavelength reflecting the visible absorption maximum.

The difference is small. Moreover, as shown in Table 4, the calculated visible absorption maximum increases with decreasing $OWF_{\pi-\pi}$ value. Because the value of $OWF_{\pi-\pi}$ decreases, the degree of π-electron delocalization increases, and the degree of molecular conjugation increases. That is, electron cloud transfers from the center of the molecule to the surroundings, which results in the increase of the electron cloud density of the nitrogen atoms, and consequently the visible absorption maximum shifts to a longer wavelength.

The electronic transitions corresponding to the calculated absorption maxima of 656.9 nm and 656.8 nm when $OWF_{\pi-\pi} = 0.793$ are listed in Table 5. As shown in Table 5, the calculated absorption maxima of 656.9 nm and 656.8 nm correspond to the electronic transitions from a_{1u} to e_g^L and a_{1u} to e_g^H, respectively. It is consistent with the well-known facts of phthalocyanine dyes absorption. Molecular orbital a_{1u} mainly consists of carbon atoms around N10, one of the covalently bonded nitrogens. The molecular orbital e_g^L mainly consists of carbon atoms around N9, the other covalently bonded nitrogens. The molecular orbital e_g^H mainly consists of carbon atoms around N8 and N11, the coordinately bonded nitrogens. Therefore, the electronic transition from regions around one covalently bonded nitrogen to those around the other covalently bonded nitrogen and the two coordinately bonded nitrogens (i.e. the transition from a_{1u} to e_g^L and e_g^H) results in the visible absorption maximum of phthalocyanine compounds.

4. Conclusions

The geometrical molecular structure of CoPc was optimized using the semi-empirical PM3 method; the results consistent with the experimental values. Based on the optimized structure, the visible absorption maximum was calculated using the ZINDO/S method. By setting $OWF_{\pi-\pi}$ at 0.793, the visible absorption maximum of CoPc was precisely predicted. The visible absorption maximum of phthalocyanines originates from the electronic transition from the π-orbital to the π*-orbital. The splitting of the visible absorption maximum results from the splitting of the doubly degenerated molecular orbital e_g. These results are helpful in improving the accuracy of visible absorption spectrum prediction and reveal the relationship between visible absorption spectrum and molecular structure. They may help in the design of molecular structures of phthalocyanine dyes.

Table 5
The electronic transition corresponding to the calculated absorption maximum

λ/nm[a]	*f*[b]	Electron transition
656.90	0.338	a_{1u} -> e_g^L
656.80	0.338	a_{1u} -> e_g^H

[a] The calculated absorption maxima when $OWF_{\pi-\pi} = 0.793$.
[b] Oscillator strength.

Acknowledgments

This work was supported by the National High Technology Research and Development Program of China (No. 2004AA009992).

References

[1] Moser FH, Thomas AL. The phthalocyanines, vols. 1 and 2. Boca Raton, FL: CRC Press; 1983.
[2] Zhao Aidi, Li Qunxiang, Chen Lan, Xiang Hongjun, Wang Weihua, Pan Shuan, et al. Science 2005;309:1542.
[3] Cotter D, Manning RJ, Blow KJ, Ellis AD, Kelly AE, Nesset D, et al. Science 1999;286:1523.
[4] Perry JW, Mansour K, Lee I-YS, Wu X-L, Bedworth PV, Chen C-T, et al. Science 1996;273:1533.
[5] Falk JE. Porphyrins and metalloprophyrins. Amsterdam: Elsevier; 1964.
[6] Achar BN, Jayasree PK. Synth Met 2000;114:219.
[7] Griffths J, Schofield J. Dyes Pigments 1997;33:65.
[8] Zagal JH. Coord Chem Rev 1992;119:89.
[9] Sakamoto Keiichi, Kato Taku. Dyes Pigments 2005;64:63.
[10] Gong XD, Xiao HM, Tian H. J Mol Struct (Theochem) 2002;593:93.
[11] Arslanoglu Yasin, Sevim AltugMert. Dyes Pigments 2006;68:129.
[12] Kobayashi Nagao. J Porphyrins Phthalocyanines 1999;4:345.
[13] Ohnholz DH, Steinbrecher S, Hanack M. J Mol Struct 2000;521:231.
[14] Matsuoka M. Infrared absorbing dyes. New York: Plenum Press; 1990.
[15] Tian H, Chen KC. Dyes Pigments 1995;27:191.
[16] Leznoff CC, Lever ABP. Phthalocyanines properties and application. New York: VCH Publishers; 1993.
[17] Almgren T, Hagstram I. Water Res 1974;8:395.
[18] Fischer H, Schulz-Ekloff G, Wohrle D. Chem Eng Technol 1997;20:624.
[19] Collins RA, Mohammed KA. J Phys D 1988;21:142.
[20] Hamann C, Hietschold M, Mrwa A, Mueller A, Starke M, Kilper R. Top Mol Organ Eng 1991;7:129.
[21] Pan Y, Chen WX, Lu SF, Zhang YF. Dyes Pigments 2005;66:115.
[22] Sun-li Mho, Bertha Ortiz, Su-Moon Park, David Ingersoll, Narayan Doddapaneni. J Electrochem Soc 1995;142:1436.
[23] Figgis BN, Kucharski ES, Reynolds PA. J Am Chem Soc 1989;111:1683.
[24] Rosa A, Baerends EJ. Inorg Chem 1994;33:584.
[25] Reynolds Philip A, Figgis Brian N. Inorg Chem 1991;30:2294.
[26] Lu X, Hipps KW, Wang XD, Mazur Ursula. J Am Chem Soc 1996;118:7197.
[27] Anderson WP, Cundari TR, Zerner MC. Int J Quantum Chem 1991; 39:31.
[28] Yuan SF, Chen ZR. J Phys Chem A 2005;109:2582.
[29] Edwards L, Gouterman M. J Mol Spectrosc 1970;33:292.