Dyes and Pigments **24** (1994) 113–124

Colour and Constitution Relationships in Organic Pigments. Part 3—Phthalocyanines

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(Received 23 September 1993; accepted 21 October 1993)

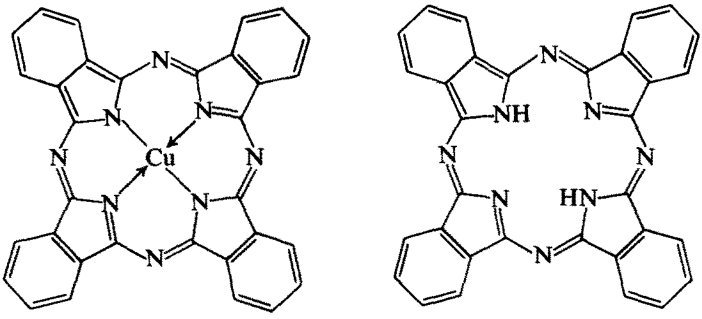
ABSTRACT

Phthalocyanines provide the most important classical organic pigments in the blue and green shade area and some derivatives are of interest as near infrared absorbers. The results of PPP molecular orbital calculations, after refinement by parameter optimisation, were found to provide good agreement with experimental λ_{max} values for a range of metal-free phthalocyanines and their complexes. The nature of the electronic excitation processes are discussed in terms of the calculated changes in π-electron charge density.

1 INTRODUCTION

Since their discovery, phthalocyanines have become one of the most extensively studied classes of compounds because of their unique structure, their extremely high stability and their potential for commercial exploitation.[1-4] In this last respect, copper phthalocyanine, CI Pigment Blue 15 (1) (Scheme 1) is of particular significance as by far the most important blue pigment, finding extensive use in the coloration of paints, printing inks and plastics. The product owes its dominant position in these applications to its brilliant blue colour, high tinctorial strength, and its exceptional fastness to light, weathering, heat, solvents, acids and alkalis. In addition, the pigment is relatively inexpensive, since in spite of the complexity of its structure, it may be synthesised in high yield from low cost starting materials. There are a number of other phthalocyanine pigments of

Dyes and Pigments 0143-7208/94/$07.00



(1) (2)

Scheme 1.

commercial importance, the colours of which are restricted to the blue and green shade areas. These include the greenish-blue metal-free compound (2), CI Pigment Blue 16, and a range of halogenated copper phthalocyanines (CI Pigment Greens 7 and 36) which exhibit a similar technical performance to copper phthalocyanine and dominate the green shade area for pigment applications. In recent years there has been an increasing interest in extending the absorption band of phthalocyanines into the near infrared region of the spectrum for a range of potential functional applications including optical data storage and security printing.[5] Some success in this respect has been achieved for example by benzannulation[5] or by incorporation of multiple arylthio substituents.[6,7]

The PPP MO method has emerged as a useful tool for the prediction of the electronic spectral properties of organic colourants.[8-10] As an example, the method has been used to provide an excellent account of the solution spectra of a series of monoazo and disazo pigments.[11,12] This paper presents the results of an investigation using the PPP molecular orbital approach into the relationship between the molecular structure of phthalocyanines and their electronic spectral properties, and describes the development of structural models which offer potential for the prediction of the spectra of phthalocyanines.

2 RESULTS AND DISCUSSION

The electronic spectra of metal phthalocyanines in solution generally show a single intense absorption band with an absorption maximum in the range 670–720 nm depending on the nature of the central metal atom. For example, copper phthalocyanine (1) in 1-chloronaphthalene gives

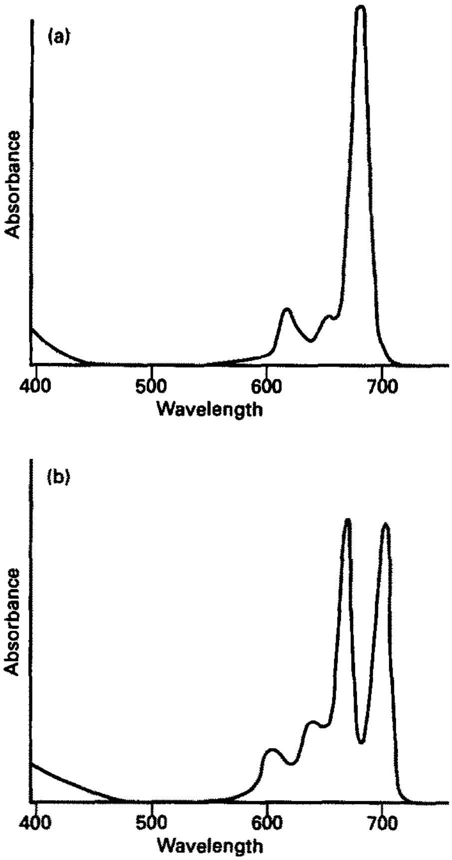


Fig. 1. Electronic absorption spectra of: (a) copper phthalocyanine (**1**); (b) metal-free phthalocyanine (**2**) in 1-chloronaphthalene.

the spectrum shown in Fig. 1(a), with a λ_{max} at 678 nm. The spectrum of metal-free phthalocyanine (**2**) (Fig. 1(b)), in contrast, shows two strong visible absorptions (λ_{max} 699, 664 nm). An explanation which has been put forward for these differences is that in the case of the metal-free compound there are two separate electronic transitions, while in the metal complex the energy levels combine into a single doubly degenerate level as a result of the enhanced symmetry of the metal complex compared with the metal-free compound.[13] The weaker absorptions at lower wavelengths in the visible spectra of the phthalocyanines are probably vibrational in origin.

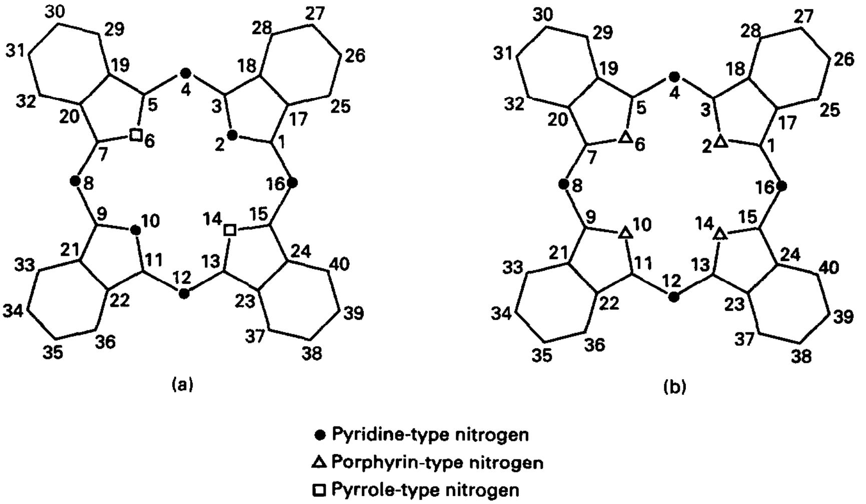
Theoretical studies of phthalocyanines using the PPP MO approach have been reported previously, although none of these had the specific aim of providing a quantitative correlation with spectral properties.[14–16] For the purposes of this present study, the theoretical investigation by

Weiss *et al.*[15] on phthalocyanine and related compounds appeared to offer an attractive starting point for the selection of parameters.[13] One-centre repulsion integral values of 10·60 eV and 13·31 eV for carbon and nitrogen respectively were used, together with a value of −11·22 eV for the valence state ionisation potential of carbon. In addition, the relationship shown in eqn (1) was proposed for the valence state ionisation potentials of the heterocyclic nitrogen atoms.

$$(\mathrm{VSIP})_\mathrm{N} = -34{\cdot}31 + 11{\cdot}05\,n \tag{1}$$

$n = 1$ for pyrrole-type N,
$n = 1{\cdot}5$ for porphyrin-type N,
$n = 2$ for pyridine-type N.

Two structural models for phthalocyanine were investigated. In the first model (Fig. 2(a)), selected to represent metal-free phthalocyanine, a structure with D_{2h} symmetry was adopted with two opposite internal nitrogens of the π-excessive pyrrole-type and the remaining six nitrogen atoms of the π-equivalent pyridine type. In the second model, selected to represent metal complex phthalocyanines, a structure with D_{4h} symmetry was adopted in which each of the four internal nitrogen atoms was assumed to be of the porphyrin type, with the six π-electrons distributed equally amongst the four atoms, and with each of the external atoms of the pyridine type. In this model, no allowance was made for the presence of the metal atom. For the initial PPP MO calculations, the valence state ionisation potentials and one-centre repulsion integrals



(a) (b)

Fig. 2. Structural models (with numbering system) for phthalocyanine.

TABLE 1

Comparison of Experimental and Calculated Electronic Spectral Data for PcH_2 (**2**) and MPc [with CuPc (**1**) as the Example]

Compound	λ_{max} *(nm) (expt)*	*Results of PPP calculations*	
		Weiss' parameters λ_{max} *(nm)* (f_{osc})	*Modified parameters* λ_{max} *(nm)* (f_{osc})
2	699 664	588 (1·60), 571 (1·72)	704 (1·91), 662 (1·46)
1	678	584 (1·69), 584 (1·69)	693 (1·74), 693 (1·74)

for carbon and nitrogen given by Weiss were used. All bond resonance integrals, to which some preliminary calculations had been found to be relatively insensitive, were fixed for simplicity at −2·4 eV. In each structural model, standard bond lengths were used, and the bond angles adjusted to reflect the appropriate molecular symmetry.

The results of these initial calculations are given in Table 1. It is of interest that the use of the first model (Fig. 2(a)) predicts two visible absorption bands with significant oscillator strengths, as is observed experimentally in the spectrum of metal-free phthalocyanine, although the λ_{max} values are approximately 80 nm too low. Further, when the more symmetrical second structural model (Fig. 2(b)) was used, absorption wavelengths of a similar order of magnitude were calculated and the degeneracy of the electronic transitions, which is observed with metal phthalocyanines, was correctly predicted. Subsequently, it was found that when the values of the valence state ionisation potential for the nitrogen atoms were amended to those given by eqn (2), an empirically-modified version of eqn (1), good agreement was obtained between the calculated and experimental λ_{max} values for metal-free phthalocyanine using the first structural model. In addition, using these modified parameters, the degeneracy predicted by the more symmetrical second model was retained and a λ_{max} value of 693 nm was obtained, which is reasonable for the range of unsubstituted metal phthalocyanines.

$$(\mathrm{VSIP})_N = -38{\cdot}91 + 11{\cdot}05n \qquad (2)$$

The calculated π-electron charge densities for the ground state and the first two excited states of phthalocyanine using both structural models based on the atom-numbering system shown in Figs 2(a) and 2(b) are given in Tables 2 and 3 respectively. Using the first model, the ground-

TABLE 2

Calculated π-Electron Charge Densities for Metal-free Phthalocyanine (2) (Based on Structural Model in Fig. 2(a)

Atom	*π-electron charge density*		
	Ground state	*First excited state*	*Second excited state*
1,3,9,11	0·71	0·65	0·75
2,10	1·51	1·54	1·51
4,8,12,16	1·42	1·46	1·43
5,7,13,15	0·78	0·78	0·72
6,14	1·81	1·81	1·82
17,18,21,22	1·01	1·00	1·04
19,20,23,24	1·02	1·05	1·02
25,28,33,36	1·00	0·95	0·96
26,27,34,35	0·99	0·99	1·01
29,32,37,40	0·96	0·95	0·94
30,31,38,39	0·99	1·00	0·98

TABLE 3

Calculated π-Electron Charge Densities for Metal Phthalocyanines (Based on Structural Model in Fig. 2(b)

Atom	*π-electron charge density*		
	Ground state	*First excited state*	*Second excited state*
1,9	0·72	0·72	0·69
2,10	1·69	1·69	1·70
3,11	0·73	0·76	0·65
4,12	1·42	1·44	1·47
5,13	0·73	0·69	0·72
6,14	1·69	1·70	1·69
7,15	0·73	0·65	0·76
8,16	1·42	1·47	1·44
17,21	1·02	1·05	1·01
18,22	1·02	1·04	1·02
19,23	1·02	1·01	1·05
20,24	1·02	1·02	1·04
25,33	0·96	0·95	0·95
26,34	0·99	1·01	0·98
27,35	0·99	1·00	0·99
28,36	0·96	0·96	0·94
29,37	0·96	0·95	0·95
30,38	0·99	0·99	1·01
31,39	0·99	0·99	1·01
32,40	0·96	0·94	0·96

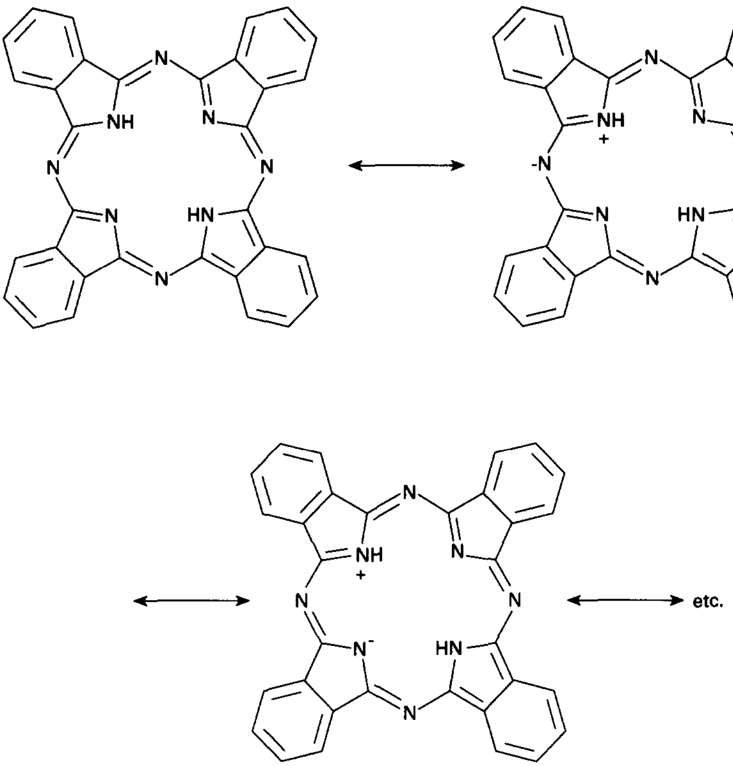
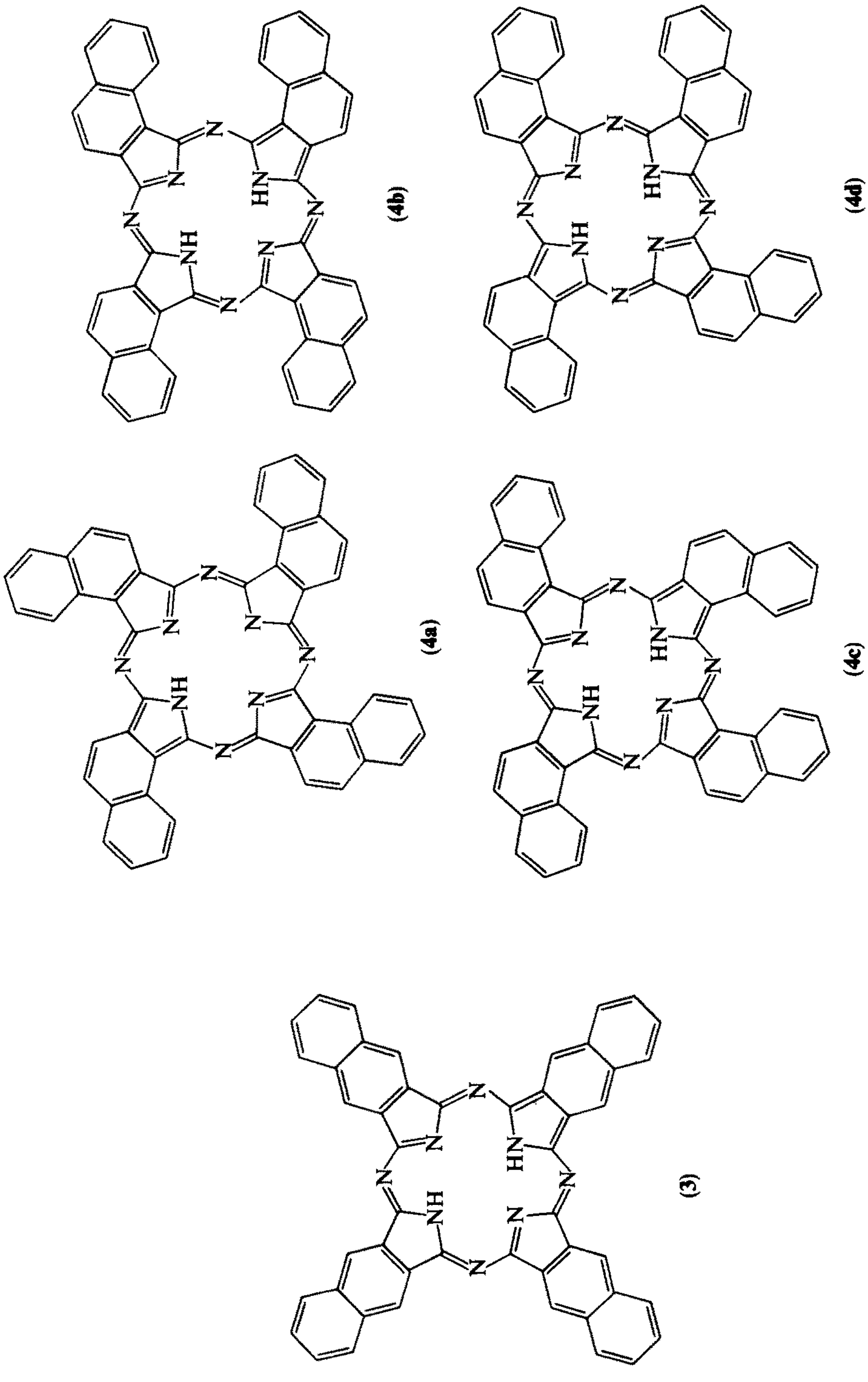


Fig. 3. Some representative canonical forms of phthalocyanine (**2**).

state charge densities are in general agreement with the valence bond approach to the bonding in metal-free phthalocyanine illustrated in Fig. 3, for example in terms of the decrease in charge density on the π-excessive nitrogens (N–6 and N–14 in Fig. 2(a)) and the increase in charge densities of the π-equivalent nitrogens (N–2, N–4, N–8, N–10, N–12 and N–16). Using this model, excitation to the first excited state was found to result in a significant increase in charge density on the π-equivalent nitrogens, together with a decrease in charge density on the carbon atoms of the two isoindoline rings which contain the π-equivalent nitrogens, notably C–1, C–3, C–9, C–11, C–25, C–28, C–33 and C–36. The second excitation involves mainly transfer of charge between carbon atoms, resulting in an overall increase in charge density in the two isoindoline rings containing the π-equivalent nitrogens and a decrease in charge density in the remaining two isoindoline rings. In both excited states, the D_{2h} symmetry of the ground state is retained. In the case of the second more symmetrical model represented by Fig. 2(b), excitation results in the loss of the D_{4h} symmetry which is shown by the ground



(4a)

(4b)

(4c)

(4d)

(3)

Scheme 2.

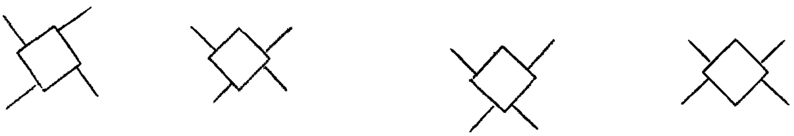
TABLE 4
Comparison of Experimental and Calculated Electronic Spectral Data for Naphthalocyanines

Compound	λ_{max} *(nm) (expt)*	λ_{max} *(nm)* (f_{osc}) *(PPP calc.)*
3	765[17]	757 (2·16), 742 (1·54)
4a		730 (1·60), 671 (1·29)
4b		731 (1·46), 663 (1·28)
4c		722 (1·54), 666 (1·26)
4d		722 (1·55), 666 (1·27)
4 (average)	720 677[18]	726 (1·54), 667 (1·28)

state. Inspection of the calculated π-electron charge densities (Table 3) illustrates that the first two excited states are identical, which is consistent with the degeneracy of the electronic transitions.

As a test of the validity of the approach using the structural model shown in Fig. 2(a) for the quantitative prediction of the λ_{max} values of metal-free phthalocyanines, calculations were extended to the naphthalocyanines. The results of the calculations (Table 4) were found to show reasonable agreement with the reported literature data. For 2,3-naphthalocyanine (**3**) (Scheme 2) which exists as a single isomer, absorptions at 757 and 742 nm are predicted, in reasonable agreement with a reported experimental value for the longest wavelength band of 765 nm.[17] The situation with 1,2-naphthalocyanine (**4**) is complicated by the four isomeric possibilities (**4a**—**d**). The compound is correctly predicted to be less bathochromic than compound **3**, the four possible isomers giving rise to a calculated absorption maximum for the longest wavelength band of between 722 and 731 nm compared with a reported experimental value 720 nm for a product which is presumably a mixture of the four isomers.[18]

In order to test the validity of the approach using the structural model shown in Fig. 2(b) for the prediction of λ_{max} values for phthalocyanine complexes, calculations were carried out on some chlorophthalocyanine copper complexes for which literature data were available.[19] Table 5 shows the correlation which was obtained between the experimental and calculated spectral data. Provided that due account is taken of all the isomeric possibilities (see Fig. 4) by comparison with an appropriate statistical average of the calculated λ_{max} values, the method provides a reasonable account of the experimental λ_{max} values. For example, it explains the enhanced bathochromic shift which is given by substitution at the 3-position compared with that of the 4-position.



(I) (II) (III) (IV)

Fig. 4. Isomer orientation in tetra-substituted phthalocyanines.

TABLE 5
Comparison of Experimental and Calculated Electronic Spectral Data for some Chlorophthalocyanines[19]

Compound		λ_{max} *(expt) (nm)*	λ_{max} *(PPP calc) (nm)* (f_{osc})
CuPc		678	693 (1·74)
Tetra-3-ClCuPc	(I)		696 (1·75)
	(II)		702 (1·75)
	(III)		705 (1·75)
	(IV)		709 (1·75)
Average		686	703 (1·75)
Tetra-4-ClCuPc	(I)		699 (1·75)
	(II)		698 (1·74)
	(III)		693 (1·73)
	(IV)		698 (1·74)
Average		679	697 (1·74)
Hexadecachloro CuPc		720	720 (1·76)

3 CONCLUSIONS

A relatively straightforward practical system for the prediction of the electronic absorption spectra of phthalocyanines using the PPP MO method has been devised and, which provides a reasonable correlation with experimental data for a series of benzannulated and substituted molecules. The method may be used, for example, to investigate the possibility of extending the available shade range of phthalocyanines absorbing in the visible region of the spectrum, and to predict synthetic target molecules for optimised near infrared absorbing properties.

4 EXPERIMENTAL

UV/visible spectra were recorded using a Perkin Elmer Lambda 2 spectrophotometer for solutions in 1-chloronaphthalene. A standard PPP-MO procedure was used within the fixed β approximation.[8] Two-centre repulsion integrals were determined by the Nishimoto–Mataga relationship.[20] Electronic excitation energies were obtained both in the absence of configuration interaction and also using a limited configuration interaction treatment involving nine singly-excited configuration obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals. In the case of the calculations on phthalocyanine based on the structural model shown in Fig. 2(a), the results given in Tables 1 and 4 were obtained following the configuration interaction treatment, which produced a useful refinement of the excitation energies. In the case of the calculations based on the structural model illustrated in Fig. 2(b), the results given in Tables 1 and 5 were obtained in the absence of configuration interaction. The configuration interaction treatment using this latter model produced rather erratic results, frequently resulting in excessively bathochromic predictions and a loss of the degeneracy. The origin of this inconsistency has not been fully established, but appears to be associated with the selection of the limits of the configuration interaction.

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