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Colour and Constitution Relationships in Organic Pigments. Part 5: The Influence of Solvents, the Central Metal Atom and Substituents on the Electronic Spectra of Phthalocyanines

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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. In this paper, the influence of solvents, and the nature of the metal atom and substituents on the solution electronic spectra of a wide range of phthalocyanines is discussed. Correlation with the results of PPP MO calculations is reported where appropriate. From this series of publications, a comprehensive understanding of the relationship between the colour and the molecular structure of phthalocyanines has emerged.

1 INTRODUCTION

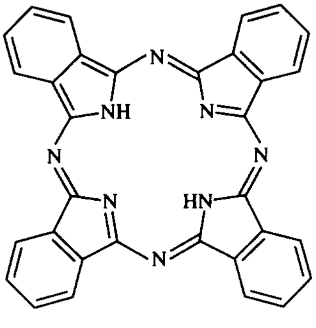
Phthalocyanines owe their dominant position as blue and green pigments to their intense absorption at long wavelengths of the visible spectrum, to their excellent durability and their relatively low cost.[1–4] In addition, a number of phthalocyanines show intense absorption in the near infrared region of the spectrum and are therefore of interest for a range of potential functional applications, including optical data storage and security printing.[5] This paper is the third in a series aimed at establishing the relationship between the molecular structure of phthalocyanines and their electronic spectral properties. In the first paper, we reported on the application of the PPP MO method, using a relatively simple but effective approach to parameterization, to the prediction of the spectral properties of a range of substituted and benzannulated phthalocyanines.[6] The mechanism of the excitation process was also discussed. In the second paper, we reported that a good correlation was obtained between the results of the PPP MO calculations and the UV/visible spectral data for a series of specifically synthesized substituted metal-free phthalocyanines.[7] This paper provides an account of the effect of some further parameters on the electronic spectra of phthalocyanines, namely the influence of solvents and the nature the central metal atom, together with some further discussion of substituent effects. The paper makes use of an extensive range of spectral data obtained both from within our laboratories and also from wider literature, and for this purpose a Russian publication containing an extensive tabulation of spectral data for phthalocyanines has proved of immense value.[8] Correlation with the results of PPP MO calculations is also reported where appropriate.

2 RESULTS AND DISCUSSION

2.1 Solvatochromism

Ideally, the interpretation of electronic spectra in terms of molecular structural effects should make use of data obtained in a single common solvent, to avoid the complication of solvent effects. However, since this publication makes use of data on phthalocyanines from a wide range of literature sources in which a variety of solvents were used, a discussion of solvent effects is appropriate. The extreme insolubility of many phthalocyanines in most organic solvents is a feature of considerable importance in their application as pigments but presents difficulties in the evaluation of the effect of solvents on their spectra. The most definitive studies have been carried out on phthalocyanines containing four tertiary-butyl substituents, which provide adequate solubility in a range of solvents.[8–10]

Table 1 gives the spectral data for some significant compounds. For the tetra-4-*t*-butyl metal free derivative, which gives a spectrum in 1-chloronaphthalene essentially superimposible on that of the parent compound (**1**), an extensive investigation of solvent effects has been reported.[9] Some selected values are shown in Table 1. For this compound, the absorption maxima of the principal absorption bands are found to be relatively insensitive to solvent effects. In particular, only a marginal bathochromic shift is observed as the polarity of non-aromatic organic solvents is increased. This observation is consistent with the results of our PPP MO calculations, which demonstrate that the symmetry of the phthalocyanine



(1)

system leads to the absence of any dipole moment in either the ground state or the excited states. The absorption bands of this compound are subject to a slightly more significant bathochromic shift in aromatic solvents, due probably to π–π interactions.

By way of comparison, Table 1 also gives the data for metal-free phthalocyanine (**1**) and for some structurally-related metal derivatives. Although the set of data available for these compounds is more limited, it is consistent with a similar trend in terms of the effect of solvents. The results of PPP MO calculations based on our previously-developed approach,[6] which does not allow for either the presence of alkyl substituents or the nature of the central metal atom, are also given in Table 1. For metal-free phthalocyanine, the λ_{max} values for the two main visible bands (Q-bands) and for the Soret band are calculated reasonably accurately. Table 1 illustrates that for tetra-4-*t*-butylphthalocyanine, molar extinction coefficients are affected more significantly by solvents than are the absorption maxima. Oscillator strengths for the three absorption maxima calculated using our optimized PPP MO method are in reasonable qualitative agreement with the experimental molar extinction coefficients.

2.2 Effect of central metal atom

In our previous paper,[6] a method was devised using the PPP MO approach for the calculation of the electronic spectra of metal phthalocyanines using a structural model with D_{4h} symmetry for which no allowance was made for the metal atom. The method successfully accounted for the single electronic transition which gives rise to the intense visible absorption band, and predicted a λ_{max} value of 693 nm. Phthalocyanine derivatives of most metals in the periodic table have now been prepared, although there is no consistent set of electronic spectral data available for all the derivatives in a single solvent.

TABLE 1
Electronic Spectral Data for Some Phthalocyanines in Various Solvents

Solvent	λ_{max} *(nm) (ε × 10⁻⁵ l mol⁻¹ cm⁻¹)*					
	$4\text{-}Bu^t_4PcH_2$[9]	PcH_2[6,11,12]	$4\text{-}Bu^t_4CuPc$[8,10]	$CuPc$[6,12]	$4\text{-}Bu^t_4VOPc$[8,10]	$VOPc$
n-Pentane	695 (1·62), 654 (1·10), 340 (0·72)					
n-Hexane	695 (2·14), 654 (1·29), 338 (0·79)		671			
Propan-1-ol	697 (0·85), 658 (0·83), 336 (0·66)					
Butan-1-ol	698 (1·02), 660 (0·93), 338 (0·71)					
DMSO	698 (1·05), 666 (1·05), 342 (0·58)		675		692	
Toluene	699 (1·82), 662 (1·51), 345 (0·69)		677		698	
Pyridine	700 (1·55), 665 (1·41), 345 (0·72)	694, 659, —				
1-Chloronaphthalene	703 (1·66), 668 (1·45), 345 (0·69)	698, 665, 350	684	678	707	701
PPP (calc.)	704 (1·91)^a, 662 (1·46)^a, 350 (0·25)^a				693	

^{a} (oscillator strength).

In the first column of Table 2, data are presented for unsubstituted metal phthalocyanines, for a range of significant metals, using 1-chloronaphthalene as solvent. The vanadyl and zinc derivatives were prepared in our laboratories in order to obtain the data which were not available from the literature. The effect of the metal atom on the λ_{max} value of the main visible absorption band is significant, the values extending from 652 to 714 nm. In the first transition series, FePc is least bathochromic (662 nm), while the vanadyl derivative is most bathochromic (701 nm). The comparison between NiPc, PdPc and PtPc demonstrates that a pronounced hypsochromic shift of the absorption band occurs on proceeding progressively to the second and third transition series. Lead phthalocyanine is the most bathochromic of the series (714 nm).

2.3 Substituent effects

Table 2 shows an extensive set of λ_{max} values for a range of substituted derivatives, all reported for solutions in aromatic solvents. The table illustrates that similar trends exist for the influence of the central metal atom on the spectra of substituted derivatives compared with its effect on the unsubstituted complexes. For example, the vanadyl derivatives are consistently the most bathochromic of the first transition series, displaying λ_{max} values of a similar order of magnitude as the longest wavelength band of the metal-free derivatives. Other observations which may be made are that the cobalt and nickel complexes generally show similar λ_{max} values, as do the copper and zinc complexes.

In previous publications, we have reported that a good correlation may be obtained between the results of optimized PPP MO calculations and the experimental spectral data for a series of substituted metal-free phthalocyanines[7] and for a series of chlorinated copper complexes.[6] The approach to the calculation of the spectra of substituted derivatives recognizes that the compounds will exist as mixtures of the four possible isomers, by obtaining an appropriate statistically weighted average of the calculated λ_{max} values. Inspection of the data in Table 2 illustrates that substituents almost invariably cause a bathochromic shift of the absorption band of phthalocyanines. In general, substituents in the 3-position give rise to larger bathochromic shifts than in the 4-position, an effect consistent with the results of PPP MO calculations. An exception to this observation is provided by the tetra-3-nitro derivatives, which are hypsochromic compared with the corresponding 4-isomers. It has been suggested that this anomalous result may be due to steric constraints forcing the nitro group out of planarity.[7]

An interesting set of compounds is the amino and dimethylamino

TABLE 2

λ_{max} Values from Electronic Spectra of Some Tetra-Substituted Phthalocyanines

Substituent	$H^{6,12-15}$	$4\text{-}Bu^{t\,8-10}$	$4\text{-}Ph^{8}$	$3\text{-}NO_2^{7,8}$	$4\text{-}NO_2^{7,8,16}$	$3\text{-}CH_3O^{7,8}$	$4\text{-}CH_3O^{8}$	$3\text{-}PhO^{7,8}$	$4\text{-}PhO^{7,8}$	$3\text{-}PhS^{7,8}$	$4\text{-}PhS^{7,8}$
PcH_2	698, 665[a]	696, 654[a]	713, 679[d]	701, 684[a]	720, 684[a]	722, 690[d]	702, 665[d]	716, 685[d]	701, 665[d]	740, 712[e]	712, 681[d]
VOPc	701[a]	707[a]	715[e]	702[a]	710[f]						
FePc	662[a]										
CoPc	672[a]	668[b]	685[e]		691[a]	692[d]	672[d]	686[d]	671[d]	710[e]	682[d]
NiPc	671[a]		683[e]	670[a]	691[a]						
CuPc	678[a]	684[a]	691[e]	680[a]	704[a]	702[d]	678[d]	694[d]	678[d]	718[e]	692[d]
ZnPc	676[a]	678[c]	694[e]	680[a]	708[a]	707[d]	680[d]	694[d]	681[d]	714[e]	692[d]
PdPc	661[a]		676[e]								
PtPc	652[a]										
PbPc	714[a]		725[e]								

[a] 1-Chloronaphthalene.
[b] 1,2-Dichlorobenzene.
[c] Benzene.
[d] 1,2,4-Trichlorobenzene.
[e] Nitrobenzene.

TABLE 3

Comparison of Experimental and Calculated λ_{max} Values (nm) for Some Tetra- and Octa-aminophthalocyanines[8]

Substituent	*3-NH$_2$*	*4-NH$_2$*	*3-NMe$_2$*	*4-NMe$_2$*	*4,4-diNMe$_2$*
VOPc	810[a]	762[a]	828[a]	775[a]	760[a]
CoPc	780[b]	730[b]		709[b]	
CuPc		720[a], 716[b]	778[b]	730[b]	730[a]
MPc (PPP calc)	775	769	826	797	869

[a] DMSO.
[b] DMF.

phthalocyanines, some spectral data for which are given in Table 3. These electron-releasing groups provide significant bathochromic shifts into the near infrared region of the spectrum, the effect being most pronounced when the substituent is at the 3-position. The results of PPP MO calculations, using standard generalized parameters for the amino and dimethylamino groups, are shown also in Table 3. The results of the calculations on the tetra-4-amino and the two dimethylamino derivatives correlate reasonably well with the experimental data for the vanadyl derivatives.

The tetra-3-amino compound is correctly predicted to be bathochromic compared with the 4-isomer, although the calculation underestimates the bathochromicity. This anomaly may well be due to the fact that an amino group in the 3-position, but not in the 4-position, is capable of intramolecular hydrogen-bonding with a heterocyclic nitrogen atom (Fig. 1), an effect not allowed for in the calculation. The calculated λ_{max} value for the octadimethylamino derivative is more than 100 nm bathochromic compared with the experimental values. This is almost certainly due to steric constraints which force the dimethylamino groups out of planarity and do not allow their full electronic effect to operate.

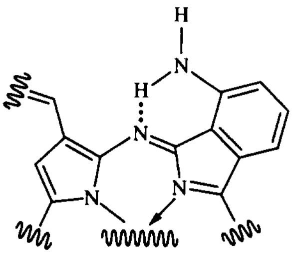


Fig. 1. Intramolecular hydrogen bonding in 3-aminophthalocyanines.

3 CONCLUSIONS

This publication provides an insight into the influence of solvents, and the nature of the metal atom and substituents on the solution electronic spectra of phthalocyanines. Together with the results reported in two previous publications,[6,7] a comprehensive understanding of the relationship between the colour and the molecular structure of phthalocyanines has emerged.

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5 EXPERIMENTAL

5.1 UV/visible spectra

UV/visible spectra were recorded using a Perkin-Elmer Lambda 2 spectrophotometer for solutions in 1-chloronaphthalene.

5.2 PPP molecular orbital calculations

A standard PPP MO procedure was used within the fixed β approximation.[17] The structural models and the parameters for the phthalocyanine ring system were as previously reported.[6,7] Literature values for the parameters for the amino and dimethylamino substituents were used.[18] Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship[19] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly-excited configurations obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals.

5.3 Synthesis of phthalocyanines

(a) Vanadyl phthalocyanine (VOPc)

Phthalonitrile (1·28 g, 0·01 mol) and vanadium (III) chloride (0·39 g, 0·01 mol) were heated at reflux in quinoline (25 cm^3) for 1 h. After cooling, vanadyl phthalocyanine (0·84 g, 58%) was obtained by filtration, and washing with ethanol and then acetone. Measured values found: C, 66·0; H, 2·7; N, 19·1%. $C_{32}H_{16}H_8VO$ requires C, 66·3; H, 2·8; N, 19·3%.

(b) Zinc phthalocyanine (ZnPc)
Phthalonitrile (12·8 g, 0·01 mol) and zinc acetate (5·6 g, 0·025 mol) were heated at reflux in quinoline (50 cm^3) for 1 h. After cooling, zinc phthalocyanine (5·27 g, 37%) was obtained by filtration, and washing with acetone, dilute hydrochloric acid and then acetone again. Measured values found: C, 66·6; H, 2·7; N, 19·4%. $C_{32}H_{16}N_8Zn$ requires C, 66·5; H, 2·8; N, 19·4%.

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