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Colour and Constitution Relationship in Organic Pigments. Part 4: Substituent Effects in Phthalocyanines

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ABSTRACT

Phthalocyanines provide the most important blue and green classical organic pigments and, in addition, some substituted derivatives are of interest for their ability to absorb in the near infrared region of the spectrum. In an investigation of substituent effects, a range of substituted metal-free phthalocyanines were prepared and their solution UV/visible spectra obtained. The results of PPP molecular orbital calculations were found to provide, in general, good agreement with experimental λ_{max} *values for the range of compounds synthesised, except for a tetranitro derivative in which steric constraints probably force the molecule to adopt a non-planar geometry.*

1 INTRODUCTION

Phthalocyanines represent 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] The parent compound (**1a**) and its copper complex are of particular importance as blue pigments, finding extensive use in the colouration of paints, printing inks and plastics. There are also a number of important phthalocyanine derivatives which contain substituents on the outer rings. For example, a range of halogenated copper phthalocyanines dominate the green shade area for pigment applications. In addition, there has been an increasing recent interest in extending the absorption band of phthalocyanines into the near infrared region of the spectrum for a range of potential

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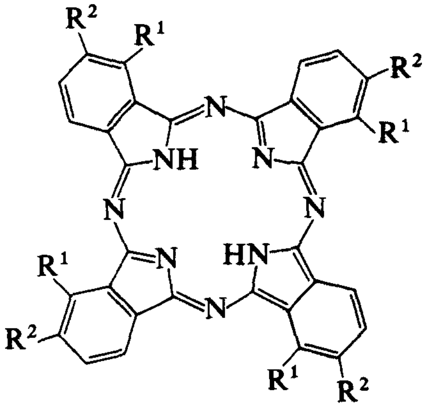
functional applications including optical data storage and security printing.[5] In particular, the incorporation of several arylthio substituents provides a significant bathochromic shift of the absorption band into the near infrared region.[6,7] In this paper, we report on an investigation into the effect of substituents on the electronic spectral properties of metal-free phthalocyanines and on the correlation obtained with the results of PPP molecular orbital calculations.



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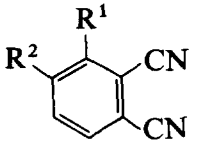

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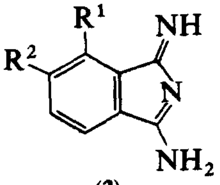

(3)

	R^1	R^2
a	H	H
b	NO_2	H
c	H	NO_2
d	OC_6H_5	H
e	H	OC_6H_5
f	SC_6H_5	H
g	H	SC_6H_5

2 RESULTS AND DISCUSSION

2.1 Synthesis and structure of substituted phthalocyanines

Following the pattern of previous work carried out in these laboratories on some azo pigments,[8,9] we elected to synthesise the parent metal-free phthalocyanine **1a**, together with a range of tetra-substituted derivatives **1b–1g**. These phthalocyanines were selected to allow systematic investigation of the influence of the electronic character of the substituent and its position of substitution on the UV/visible spectral properties of the compounds.

The method of synthesis of phthalocyanines may be classified broadly into two groups:

(a) from phthalic acid derivatives by direct tetramerisation/cyclisation;
(b) from metal complex phthalocyanines by acid replacement.

A range of derivatives of phthalic acid may be converted into phthalocyanine (**1a**), including phthalonitrile (**2a**) and *o*-cyanobenzamide, the latter being a readily available material favoured by Linstead in his early work.[10] However, there is now a wide range of substituted phthalonitriles which may be relatively easily prepared and these are attractive precursors of substituted phthalocyanines. For the conversion of phthalonitriles to phthalocyanines, a method reported by Brach appeared to offer certain advantages, notably in terms of yield and product purity.[11] This method involves reaction of the phthalonitrile (**2**) with ammonia and sodium methoxide in methanol to form the 1-amino-3-iminoisoindoline (**3**), which is subsequently converted to the phthalocyanine (**1**) in refluxing 2-N,N-dimethylaminoethanol. It was found that phthalonitriles (**2a–2g**) were in each case smoothly converted to the 1-amino-3-iminoisoindoline (**3a–3g**). Subsequently, from the appropriate aminoiminoisoindoline intermediates, phthalocyanines (**1a**) and (**1c–1g**) were prepared in satisfactory yield. However, attempts to convert the 3-nitro derivative (**3b**) to the corresponding phthalocyanine (**1b**) were unsuccessful, leading to low yields of a highly impure product. In this case the 3-nitro group clearly has an adverse influence on phthalocyanine formation, probably as a result of a combination of steric and electronic effects on the condensation reactions linking isoindole units.

A number of metal derivatives of phthalocyanine may be converted to the metal-free compound by acidic removal of the metal ions, most notably the alkali metal and alkaline earth derivatives. Of these the dilithium derivatives have been highlighted owing to their ease of formation and their smooth conversion to the metal-free phthalocyanine at low temperatures by acid treatment. Using this route, 3-nitrophthalonitrile (**2b**) was converted in low yield to phthalocyanine (**1b**). Satisfactory analytical data were obtained for phthalocyanines (**1a–1g**). It is recognised that while the parent compound (**1a**) will be a single component, each of the tetra-substituted derivatives (**1b–1g**) will be mixtures of the four possible isomers.[4] The infrared spectra of compounds **1a–1g** show distinct similarities and a number of features characteristic of the phthalocyanine system.[12] In particular, each of the phthalocyanines exhibit N–H stretching vibrations in the range 3090–3290 cm^{-1}, absorptions due to N–H deformations between 1005 and 1025 cm^{-1} and between 720 and 750 cm^{-1} and aromatic C–H stretching vibrations at *c.* 3000 cm^{-1}. The substituted phthalocyanines show, in addition, absorptions characteristic of the particular functional groups present.

2.2 Uv/visible spectra of the phthalocyanines

Uv/visible spectra of phthalocyanines (**1a–1g**) were obtained for solutions in 1-chloronaphthalene and the λ_{max} values are reported in Table 1. The spectra are typical of those previously reported for metal-free phthalocyanines.[4] In each case, there are two intense absorptions at long wavelengths and two much weaker absorptions at shorter wavelengths which are probably vibrational in origin. The presence of substituents causes in each case a bathochromic shift of the absorption bands relative to the parent compound (**1a**). In the case of the electron-releasing phenoxy and thiophenoxy groups, the bathochromic shift is significantly greater when the substituent is at the 3-position. In contrast, the nitro group exhibits a more pronounced effect at the 4-position. In a previous publication,[13] we reported on the application of the PPP molecular orbital approach to the prediction of the electronic spectra of phthalocyanines. A method which uses a structural model assuming the D_{2h} symmetry of structure (**1a**) and specifically-optimised parameters for the heterocyclic nitrogen atoms was found to provide a good account of the literature data for phthalocyanine and some benzannulated derivatives. The correlation between experimental λ_{max} values and the values calculated using this model for compounds **1a–1g** is shown in Table 1. For the substituted derivatives (**1b–1g**), the results given are statistically-weighted averages of the values calculated for each of the four isomeric possibilities. In each case two long wavelength absorptions with significant oscillator strengths are predicted and, in general, the calculated λ_{max} values are in reasonable agreement with the experimental data. For example, the method correctly predicts the order of bathochromicities for the phenoxy and thiophenoxy derivatives (**1d–1g**). A notable exception, however, is the nitro derivative (**1b**) for which a longest wavelength λ_{max} value some 35 nm too high is calculated. It is possible that the origin of this anomaly may be steric constraints involving interaction of the nitro groups with the lone pairs of electrons on the heterocyclic nitrogen atoms which force the nitro group out of the planarity and do not permit its full electronic effect to operate.

TABLE 1
Comparison of Experimental and Calculated UV/Visible Spectral Data for Metal-free Phthalocyanines

Compound	λ_{max} *(expt) (nm)*	λ_{max} *(PPP calc) (nm)* (f_{osc})
1a	699, 664, 635, 602	704 (1·91), 666 (1·46)
1b	702, 668, 642, 612	737 (1·96), 721 (1·38)
1c	717, 685, 651, 625	715 (2·20), 654 (1·30)
1d	722, 692, 659, 626	727 (1·84), 667 (1·41)
1e	707, 674, 645, 613	725 (1·86), 681 (1·62)
1f	742, 717, 679, 648	731 (1·86), 682 (1·49)
1g	719, 688, 657, 624	716 (2·00), 691 (1·48)

3 CONCLUSION

The use of the PPP MO method using a model previously optimised for metal-free phthalocyanines provides a good account of a range of substituent effects tested on a number of specifically-synthesised derivatives with the exception of a tetranitro derivative in which steric constraints probably force the molecule to adopt a non-planar geometry. The approach offers considerable potential for the prediction of the colouristic properties of phthalocyanines of synthetic interest. The method may be used, for example, to investigate the possibility to extend 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

4.1 Instrumental methods

Infrared spectra were recorded as KBr discs with a Perkin–Elmer 1740 Fourier Transform spectrometer. UV/visible spectra were recorded on a Perkin–Elmer Lamda 2 spectrophotometer for solutions in 1-chloronaphthalene. ^{1}H-n.m.r. spectra were recorded on a Perkin–Elmer R32 spectrometer for solutions in deuterochloroform with tetramethylsilane as internal reference. C, H and N analyses were carried out in the Department of Applied Chemical Sciences, Napier Polytechnic, Edinburgh.

4.2 PPP MO calculations

A standard PPP–MO procedure was used within the fixed β approximation.[14] The structural model and the parameters for the phthalocyanine ring system were as previously reported.[13] Literature values for the parameters for the nitro[8] and for the ether and thioether group[15] were used. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship[16] 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.

4.3 Synthesis of the phthalocyanines

4.3.1 Dinitriles (2b–g)

3-Nitrophthalonitrile (**2b**) and 4-nitrophthalonitrile (**2c**) were prepared according to literature procedures by dehydration of the diamides.[17] 3-Phenoxyphthalonitrile (**2d**), 4-phenoxyphthalonitrile (**2e**), 3-thiophenoxyphthalonitrile (**2f**) and 4-thiophenoxyphthalonitrile (**2g**), were prepared according to literature procedures by treating the appropriate nitrophthalonitrile (**2b**) or (**2c**) with either phenoxide or thiophenoxide anion.[18]

4.3.2 Phthalocyanines (1a–1g)

(a) Via 1-amino-3-iminoisoindolines. Dinitriles (**2a–g**) (0·01 mol) in methanol (25 ml) were treated with ammonia and sodium methoxide according to the method of Brach.[11] In each case a colourless or pale-yellow crystalline material separated and was isolated by filtration. Analysis by TLC indicated in each case that there was a major component present together with traces of other components. Infrared and proton n.m.r. spectra of the materials were consistent with the formation in each case of the 1-amino-3-iminoisoindolinone (**3a–3g**) as the major product formed in yields of between 30 and 72%. As a representative example, the following spectral data were obtained for the phenoxy derivative (**3d**): δ_H 3·27 (1H, s, NH), 6·9–7·8 (9H, m, ArH), 8·68 (2H, br s, NH_2); ν_{max} 3273, 3037 (N–H), 1623, 1587, 1540, 1490, 1456, 1332, 1313, 1256, 1216, 1160, 1137, 1070, 1034, 968, 880, 814, 774, 724, 698. Because of the reported instability of 1-amino-3-iminoisoindolines, the materials were used directly without further purification.

For conversion to the phthalocyanines, the 1-amino-3-iminoisoindolines (0·001 mol) were heated at reflux in 2-N,N-dimethylaminoethanol (2 ml) for 7 h.[11] The products were isolated by filtration and purified by repeated washing with hot acetone. Phthalocyanines (**1a**) and (**1c–1g**) were obtained as blue-green or green powders by this method as follows:

1a (23%): found C, 74·3; H, 3·4; N, 21·8%. $C_{32}H_{18}N_8$ requires C, 74·7; H, 3·5; N, 21·8%. ν_{max}/cm^{-1} 3274 (N–H str), 3048 (C–H str), 1500, 1438

(C–C str), 1335, 1322, 1119, 1094, 1005 (N–H def), 874 (C–H def), 751, 736 (C–H def), 720 (N–H def).

1c (30%): found C, 54·6; H, 2·1; N, 22·8%., $C_{32}H_{14}N_{12}O_8$ requires C, 55·3; H, 2·0, N, 24·2%. ν_{max}/cm^{-1} 3090 (N–H str), 2932 (C–H str), 1523 (asym nitro str), 1455 (C–C str), 1385, 1342 (symm nitro str), 1327, 1132, 1090, 1039, 1008 (N–H def), 850, 813, 800, 755, 731 (N–H def).

1d (74%): found C, 75·9; H, 3·7; N, 12·6%. $C_{56}H_{34}N_8O_4$ requires C, 76·1; H, 3·9; N, 12·7%. ν_{max}/cm^{-1} 3289 (N–H str), 30326 (C–H str), 1582, 1487, 1457, 1334, 1290, 1253 (asymm ether str), 1225, 1208, 1155, 1138, 1108, 1093, 1069, 1025, 1005 (N–H def), 957, 942, 868, 801, 750 (N–H def), 688.

1e (28%): found C, 74·9; H, 3·5; N, 13·2%. $C_{56}H_{34}N_8O_4$ requires C, 76·1; H, 3·9; N, 12·7%. ν_{max}/cm^{-1} 3290 (N–H str), 3035 (C–H str), 1615, 1589, 1541, 1522, 1507, 1490, 1474, 1420, 1397, 1338, 1321, 1231 (asymm ether str), 1163, 1113, 1093, 1011 (N–H def), 930, 863, 825, 746 (N–H def), 712, 691, 670.

1f (36%): found C, 70·4; H, 3·5; N, 11·7%. $C_{56}H_{34}N_8S_4$ requires C, 71·0; H, 3·6; N, 11·8%. ν_{max}/cm^{-1} 3284 (N–H str), 3053 (C–H str), 1594, 1567, 1497, 1473, 1439, 1398, 1329, 1311, 1270, 1234, 1221, 1176, 1142, 1119, 1082, 1066, 1023 (N–H def), 900, 874, 851, 796, 748 (N–H def), 703, 691.

1g (54%): found C, 71·0; H, 3·4; N, 11·8%. $C_{56}H_{34}N_8S_4$ requires C, 71·0; H, 3·6; N, 11·8%. ν_{max}/cm^{-1} 3289 (N–H str), 3055 (CX–H str), 1601, 1580, 1541, 1506, 1475, 1457, 1439, 1408, 1387, 1309, 1135, 1108, 1067, 1013 (N–H def), 897, 821, 800, 744, 689, 669.

Attempted synthesis of tetranitrophthalocyanine (**1b**) by this method gave a very low yield of a highly impure product.

(b) Via the dilithium derivative. Tetranitrophthalocyanine (**1b**) was obtained as a dark green powder in an overall yield of 5% from 3-nitrophthalonitrile (**2b**) via the dilithium derivative, using the method previously reported by Oliver and Smith for the preparation of the tetranitro compound (**1c**).[19] Found C, 55·1; H, 2·0; N, 23·7%. $C_{32}H_{14}N_{12}O_8$ requires C, 55·3; H, 2·0; N, 24·2%. ν_{max}/cm^{-1} 3212, 3089 (N–H str), 2922 (C–H str), 1532 (asymm nitro str), 1486, 1463 (C–C str), 1385, 1344 (symm nitro str), 1236, 1154, 1092, 1045, 1024 (N–H def), 929, 912, 817, 803, 755, 728 (N–H def).

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