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The Syntheses of Some Phthalocyanine Intermediates and Pigments

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ABSTRACT

The syntheses of various bromo and iodo derivatives of copper phthalocyanine pigments are reported; the halogenated primaries always led to trimeric or tetrameric acyclic compounds. Copper atoms were incorporated into the structures obtained from the corresponding iodinated primaries. An indirect route to the synthesis of copper tetra-3-iodophthalocyanine via the syntheses of copper tetra-3-amino- and copper tetra-3-nitro-phthalocyanine pigments is also reported.

1 INTRODUCTION

The phthalocyanine pigments comprise a class of highly coloured synthetic compounds and various metal and metal-free phthalocyanine pigments have been synthesized.[1−3] Whatever the type, all the phthalocyanines contain in common the tetrabenzoporphyrazine chromophore **I**.

Although structure **I** is a plausible formula supported by very many physical and chemical observations,[4,5] the intermediates leading to phthalocyanines have not been characterized clearly. The involvement of 3-iminophthalimidine.[6,7] 1,3-di-iminoisoindoline,[8] and 1-amino-3-imino-isoindolenine[9] has been claimed, but the mechanism has never been completely and irrefutably explained. Therefore the isolation and identification of the intermediates leading to phthalocyanines are vital for the elucidation of some mechanistically obscure points. For this reason, the cyclization of the tetrabenzoporphyrazine ring in the phthalocyanine skeleton structure has

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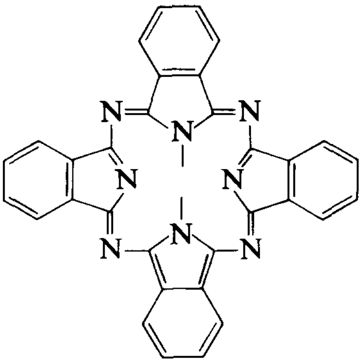


(I)

been prevented by substituting suitable groups, in suitable orientations, into the structure of phthalocyanine primaries.

2 RESULTS AND DISCUSSION

By using the PMO theory[10,11] it can be visualized, after deleting all the essentially single or double bonds from the resonance structure of the phthalocyanine molecule, that the system is isoconjugate with a $4m+2$ annulene, m being the number of carbons. Hence, tetrabenzoporphyrazine ring formation should occur accompanied by ring stabilization. However, the involvement of four isoindole units should disfavour phthalocyanine formation entropically. Thus, the course of the overall reaction is dictated by two principal but opposing factors, namely the enthalpy and the entropy of the reaction. The relative magnitudes of these thermodynamic functions are required in order to visualize the overall tendency of the primaries, i.e. whether or not they will undergo reaction in the desired direction. The aromaticity of the products is just one part of the total enthalpy changes of the reactions involved in phthalocyanine-type pigment formation. On the other hand, substituents on the primaries should exert a steric repulsive energy contribution but should not affect the reaction entropy appreciably.

In this present work, Krevelen–Chermin Gibbs free energy calculations[12] in the temperature range 300–600 K were carried out for numerous pthalocyanines having different halogen substitutents. Of these, bromine and iodine substitutions symmetrically oriented at the 3,6- and 4,5-positions were utilized for convenience. Table 1 tabulates the Gibbs free energy of formation, ΔG_f°, for various brominated and iodinated phthalocyanines as a function of temperature. It is known that the accuracy of the method is within $\pm 20{\cdot}9$ kJ mol^{-1}.[12]

The calculations imply that although the brominated primaries should

TABLE 1
Gibbs Free Energy of Formation (kJ mol^{-1}) of Various Iodo- and Bromo-phthalocyanines ($\Delta G_f^\circ = A + BT \times 10^{-2}$)

Substituents			
3,6-	*4,5-*	*A*	*B*
H	H	766·44	134·09
Br	Br	723·93	116·32
I	I	1 353·94	133·71
H	Br	713·94	125·06
H	I	1 028·94	133·76
Br	H	729·45	122·43
I	H	1 044·45	131·12

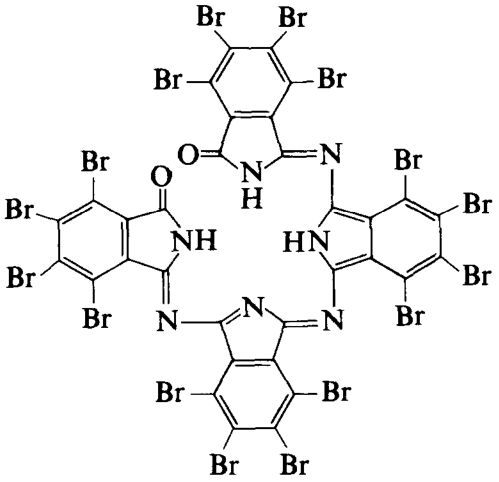
lead to the corresponding phthalocyanines thermodynamically as favourably as their unsubstituted analogues, this should not be the case for the iodinated primaries, thus allowing the isolation of certain intermediates prior to tetrabenzoporphyrazine ring formation. The Krevelen–Chermin Gibbs free energy calculations reveal that fluorinated and chlorinated phthalocyanines have much less positive ΔG_f° values compared with the unsubstituted metal-free phthalocyanine molecule.

Many polyhalophthalocyanines, mostly chlorinated, have been obtained by various direct or indirect halogenation methods.[2,4,13–15] Highly halogenated pigments have been manufactured by using mixtures of chlorine and bromine or bromination in molten aluminium chloride.[16–19] There is little information concerning bromination of copper phthalocyanine and iodo analogues.

In this present work various attempts were made to obtain halogenated phthalocyanines or intermediates directly or indirectly. For that purpose, the 'phthalic anhydride–urea' process was employed, using the 'solvent process' or 'melt process'.[1] Copper was used as the central atom.

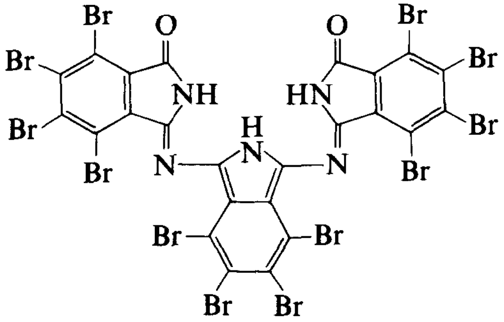
In order to accomplish the syntheses of bromo analogues of copper phthalocyanine, tetrabromophthalic anydride, obtained by the bromination of phthalic anhydride,[20] was employed in a solvent process.[1–3] Ammonia gas was passed through a solution of tetrabromophthalic anhydride in 1-bromonaphthalene in the presence of cuprous chloride and ammonium molybdate catalyst. The product, which was light green after the pigmentation process,[1–3] was shown by X-ray analysis not to contain copper. The infrared spectrum (recorded in Nujol) showed N—H stretching at 3225 cm^{-1} and symmetric and asymmetric γ-lactone bands at 1780 cm^{-1} and 1720 cm^{-1} respectively. Substituted imine bands appeared at 1705 and

1680 cm^{-1}. From an evaluation of ^{1}H-NMR and IR data in conjunction with microanalytical data, and considering the observed C/N (4·64) and Br/N (2·38) atom ratios, the tetrameric structure **(II)** is proposed.



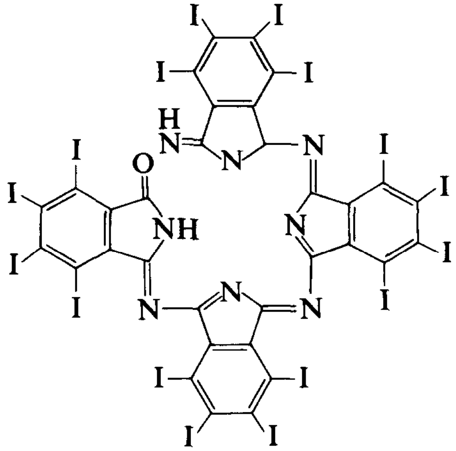
(II)

The reaction was also carried out using the melt process in the presence of urea, cuprous chloride and the catalyst. The IR spectrum (Nujol) of the product shows characteristic N—H stretching (3225 cm^{-1}), symmetric and asymmetric lactam carbonyl stretchings (1780 cm^{-1} and 1720 cm^{-1} respectively) and substituted imine stretchings (1705 and 1680 cm^{-1}). The ^{1}H-NMR spectrum showed only the resonance of N—H protons and X-ray analysis discarded any possibility of the presence of a copper atom in the molecule. The observed C/N (4·73) and Br/N (2·35) ratios imply a trimeric structure. The spectral data are thus in favour of structure **III**.



(III)

Tetraiodophthalic anhydride[20] was treated with urea in the presence of cuprous chloride and ammonium molybdate catalyst (melt process). After the pigmentation treatment a greenish-brown powder, decomposing gradually above 215°C, was obtained. The presence of N—H stretchings (3230 cm^{-1}), symmetric and asymmetric lactam carbonyl bands (1780 and 1720 cm^{-1} respectively) and an imine peak at 1630 cm^{-1} in the IR spectrum (Nujol) indicated the acyclic nature of the compound. Comparison of the theoretical and observed C/N (4·00 and 4·06) and I/N (2·00 and 1·93) atom ratios strongly favour a tetrameric structure. The ^{1}H-NMR (chloropicrin) spectrum displays only N—H protons. The absence of copper was proved by means of X-ray fluorescence. Thus, a conjugated acyclic tetrameric tetraiodophthalimide chain, linked by imine nitrogens (**IV**) is the most probable structure of the compound.



(IV)

Tetraiodophthalic anhydride, cuprous chloride and urea in 1-bromonaphthalene at 260°C was refluxed for 2 h, giving a light green product after the pigmentation process. The IR spectrum (Nujol) indicated the presence of N—H (3230 cm^{-1}), lactam carbonyl (1780 and 1720 cm^{-1}) and substituted imine (1640 cm^{-1}) structures, thus indicating that the product was an acyclic macromolecule composed of isoindole units bonded by imine nitrogens. The iodine and C, H, N analyses, together with C/N and I/N ratios, indicated the tetrameric nature of the compound. Figures 1 and 2 show the X-ray and IR spectra of the compound. The strong peak at $\phi = 42{\cdot}5°$ is indicative of a copper atom. The results obtained support the most likely structure as V.

On the other hand, tetraiodophthalic anhydride, cuprous chloride, urea and the catalyst in nitrobenzene yielded a brownish-yellow compound.

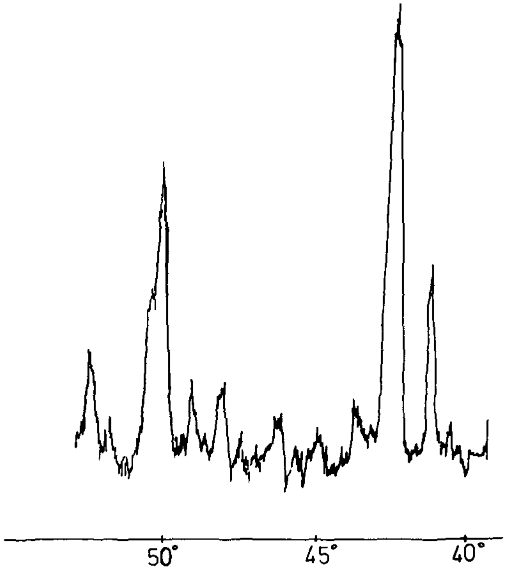


Fig. 1. X-ray fluorescence spectrum of compound **V** (Cu k ∝ :400 cps; 40 kv 1°/dak; 20 mA: 600 mm/h).

The IR spectrum (Nujol) had 3240 cm^{-1} (N—H stretching), 1780 cm^{-1}, 1720 cm^{-1} (γ-lactam stretchings) and 1700 cm^{-1} (substituted imine) bands. The presence of carbonyl and imine groups indicate an acyclic structure of isoindole units. Elemental analysis of the compound, together with the calculated and observed C/N (4·80 and 4·95) and I/N (2·40 and 2·40) ratios, suggest a trimeric structure. The presence of copper was also proved. The occurrence of a somewhat broadened N—H peak in the IR spectrum may be

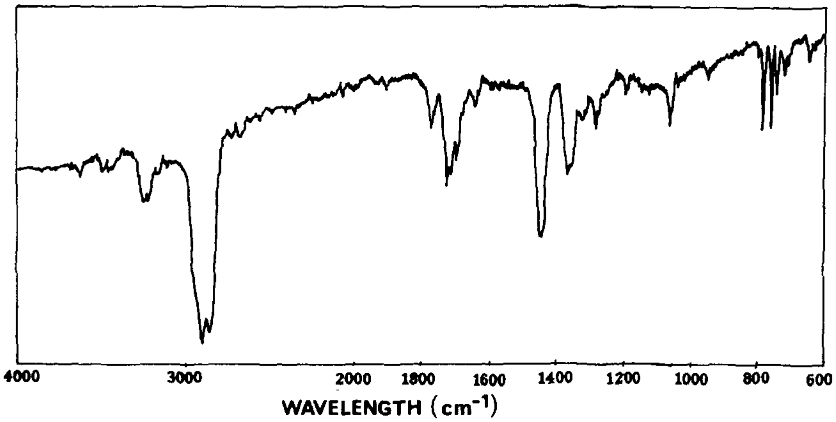
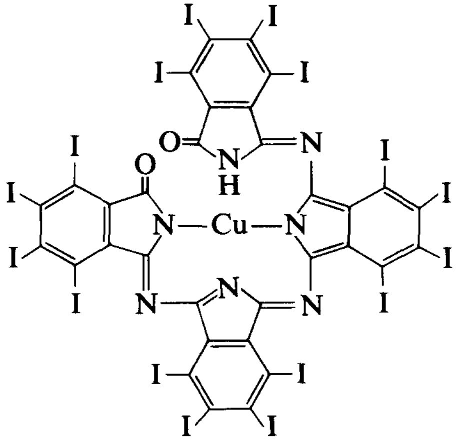
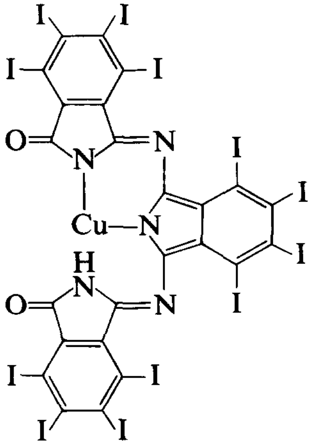
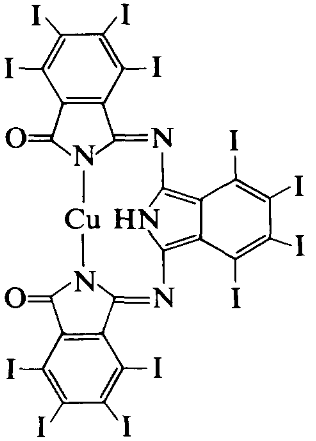


Fig. 2. Infrared spectrum of compound **V**.

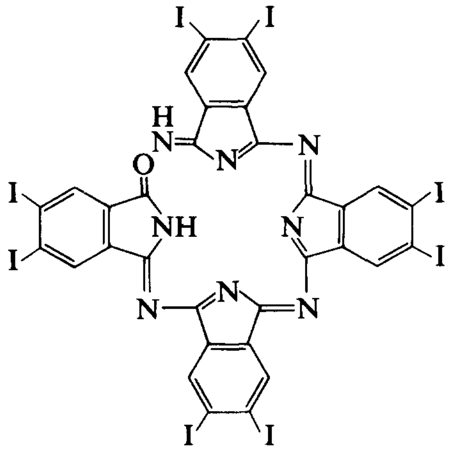

(V)

due to the existence of lactam–lactim tautomerism. Structure **VI-a** is the more probable formula of the compound.


(VIa)


(VIb)

4,5-Di-iodophthalic anhydride, urea, cuprous chloride and ammonium molybdate were subjected to the melt process and failed to produce any tetrabenzoporphyrazine skeleton. All the spectral analyses favoured structure **VII**. The IR spectrum of the product showed unsubstituted imine stretching at 3400 cm^{-1}, imide type N—H stretching at 3200 cm^{-1}, substituted imine stretching at 1598 cm^{-1} and lactam bands at 1780 and 1720 cm^{-1} (for the symmetric and asymmetric stretchings respectively). The X-ray fluorescence spectrum did not give any peak at $40° < \phi < 50°$ for the presence of copper. Moreover, the observed C/N (3·96) and I/N (0·975) atom ratios exclude the possibility of dimeric and trimeric structures.

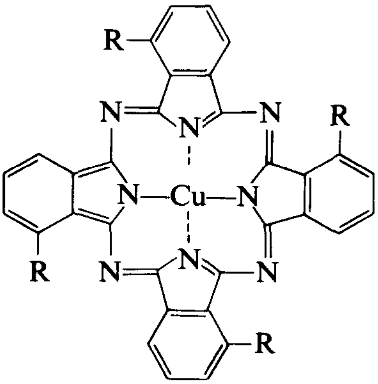


(VII)

All the halogenated phthalocyanine primaries studied in the present work resulted in acyclic trimers or tetramers, mostly high-melting (m.p. > 350°C), and were bright yellow or brownish materials which were stable to moderately strong concentrations of acids and bases.

On the other hand, direct iodination or bromination of copper phthalocyanine in the presence of peroxyacetic acid under various reaction conditions failed to produce the corresponding halogenated derivatives. However, 3-nitrophthalic anhydride yielded copper tetra-3-nitrophthalocyanine (**VIII**) which was reduced with Sn/HCl to produce the corresponding amino derivative (**IX**). Application of the Sandmeyer reaction then yielded copper tetra-3-iodophthalocyanine (**X**). X-rays analyses indicated the presence of copper in compounds **VIII** to **X**, which were all blue in their pigment form, compound **IX** being the darkest.

In the light of the above, the syntheses of iodophthalocyanines, probably



(VIII) R = NO_2, (IX) R = NH_2, (X) R = I.

because of their comparatively more positive Gibbs free energy of formation, should require indirect methods rather than direct iodination or syntheses starting from iodinated primaries. It seems that, for bromo or iodo derivatives, condensation reactions should occur in a facile manner to form trimeric or tetrameric structures, but the formation of the tetrabenzoporphyrazine ring is not favoured. In the case of acyclic structures having a 3,4,5,6-tetraiodophenylene moiety, the copper atom should be firmly bound because it is retained in the structure after subsequent acid and base treatments in the purification and pigmentation processes.

3 EXPERIMENTAL

3.1 General

The crude products obtained were treated with 20% (w/w) NaOH and then 30% (w/w) HCl, washed with distilled water several times and filtered. The product was converted into a finely powdered sample after drying with absolute alcohol. The pigment form of the powder was obtained by the acid pasting process,[1] in which 1 part of powdered sample was dissolved in 6–10 parts of concentrated sulphuric acid. The mixture was allowed to stand for 1–2 h and then was poured onto 40–50 parts of crushed ice and stirred thoroughly. The pigment thus obtained was filtered off and washed with hot water. Finally, the sample was dried repeatedly by absolute alcohol treatment and kept in a vacuum desiccator for two days.

The melting points were determined with a Reichert apparatus. Spectra were recorded with Beckman IR 18A and Perkin–Elmer 700 IR spectrometers and a Varian T-60 A NMR spectrometer. The copper was determined with a Philips PW-1300 X-ray fluorescence instrument.

Because of the insolubility of the products in common deuterated NMR solvents, chloropicrin (CCl_3NO_2) was used.

A Hewlett–Packard chromatograph was used in order to determine the C, H and N percentages. Halogen contents of the samples were obtained quantitatively by the Carius combustion method[21] and the average of three parallel runs was reported.

In all syntheses ammonium molybate was employed as catalyst.[1]

3.2 Synthesis of compound II

To a mixture of tetrabromophthalic anhydride (3·12 g, 6·72 mmol), ammonium molybdate (0·003 g, $8{\cdot}82 \times 10^{-6}$ mol) and cuprous chloride (0·150 g, 1·52 mmol), 1-bromonaphthalene (50 ml) was added and NH_3 gas was passed through while stirring the mixture. The reaction was continued at 260°C for 8 h. The green product obtained after the pigmentation (69%) decomposed above 255°C. Found: C, 20·9; H, 1·0; N, 5·25; Br, 71·5. Calculated for $C_{32}H_3N_7Br_{16}$: C, 21·4; H, 0·2; N, 5·45; Br, 71·2%.

3.3 Synthesis of compound III

A mixture of urea (6·32 g, 0·1 mol) and ammonium molybdate (0·068 g, 0·2 mmol) was melted at 140°C and tetrabromophthalic anhydride (3·88 g, 8·36 mmol) and cuprous chloride (2·23 g, 22·6 mmol) were added all at once. The mixture was heated to 200°C, stirred for 30 min and a further 4·0 g of urea was added with stirring. A brown product was obtained in 65% yield after the pigmentation process. Found: C, 21·5; H, 0·8; N, 5·3; Br, 71·2. Calculated for $C_{24}H_3N_5O_2Br_{12}$: C, 21·3; H, 0·2; N, 5·2; Br, 70·95%.

3.4 Synthesis of compound IV

Urea (1·30 g, 21·6 mmol) and ammonium molybdate (0·07 g, 0·2 mmol) were melted and a mixture of tetraiodophthalic anhydride (4·42 g, 6·77 mmol) and cuprous chloride (0·13 g, 1·31 mmol) was added at 140°C while stirring the melt thoroughly. The temperature was raised to 210°C and the mixture was left to stand at that temperature for 3 h. The pigmented product was maroon with a greenish lustre (62%). The powder decomposed gradually above 215°C. Found: C, 15·7; H, 0·7; N, 4·5; I, 79·0. Calculated for $C_{32}H_2N_8OI_{16}$:C, 15·1; H, 0·1; N, 4·4; I, 79·8%.

3.5 Synthesis of compound V

Tetraiodophthalic anhydride (4·36 g, 6·68 mmol), cuprous chloride (0·14 g, 1·42 mmol) ammonium molybdate (0·003 g, $8{\cdot}82 \times 10^{-6}$ mol) and urea (1·30 g, 21·6 mmol) were mixed in 50 ml 1-bromonaphthalene and the mixture refluxed at 260–265°C for 3 h. The purified product, obtained in 60% yield, was green in colour. Found: C, 14·95; N, 3·5; I, 76·8. Calculated for $C_{32}HN_7O_2I_{16}Cu$: C, 14·7; N, 3·75; I, 77·85%.

3.6 Synthesis of compound VI

Cuprous chloride (0·15 g, 1·52 mmol), tetraiodophthalic anhydride (4·32 g, 6·65 mmol), urea (1·30 g, 21·6 mmol) and ammonium molybdate (0·003 g, $8{\cdot}82 \times 10^{-6}$ mol) were added to 100 ml nitrobenzene and the mixture was refluxed for 4 h. The product was purified by removing nitrobenzene, digesting the crude product in absolute ethanol and pigmented by acid pasting. The product was dull brownish yellow in colour and was obtained in 65% yield. It decomposed above 230°C. Found: C, 14·9; H, 0·3; N, 3·5; I, 76·5. Calculated for $C_{24}HN_5O_2I_{12}Cu$: C, 14·6; H, 0·05; N, 3·5; I, 77·0%.

3.7 Synthesis of compound VII

4,5-Di-iodophthalic anhydride (1·55 g, 3·87 mmol) and cuprous chloride (0·1 g, 1·01 mmol) were added to melted urea (2·05 g, 34·1 mmol) and ammonium molybdate (0·016 g, $4{\cdot}70 \times 10^{-5}$ mol) at 145°C. The mixture was heated at 200°C for 2 h. The crude product was cooled to room temperature and pigmented, giving a bright green powder (60%). Found: C, 25·5; H, 0·95; N, 7·5; I, 66·3. Calculated for $C_{32}H_2N_8OI_8$: C, 25·1; H, 0·1; N, 7·3; I, 66·4%.

3.8 Synthesis of copper tetra-3-nitro phthalocyanine (VIII)

Urea (13·0 g, 0·216 mol) and ammonium molybdate (0·035 g, 0·102 mmol) were melted at 135°C and 10·2 g (52·5 mmol) 3-nitrophthalic anhydride was added. The reaction temperature was raised to 200°C and maintained for 90 min. A dark blue product (72%) was obtained after purification and pigmentation. ν_{max} (Nujol) 1530, 1380 (NO_2), 1610 cm^{-1} (substituted imine). δ (CCl_3NO_2) 8·40–7·00 ppm (m, aromatic). Found: C, 50·1; H, 1·7; N, 22·2. $C_{32}H_{12}N_{12}O_8Cu$ requires: C, 50·9; H, 1·6; N, 22·25%.

3.9 Synthesis of copper tetra-3-aminophthalocyanine (IX)

Copper tetra-3-nitrophthalocyanine (5 g, 6·62 mmol) was treated with a 4-mol equivalent excess of Sn/HCl mixture at 40–50°C for 3 h while stirring thoroughly. The mixture was left until all the hydrogen effervescence had subsided. The crude product was filtered, stirred into 50 ml concentrated HCl and refiltered. The dark blue product was further purified and pigmented (54%) as described above. ν_{max} (Nujol) 3450, 3320 (N—H stretching), 1610 cm^{-1} (substituted imine). δ (CCl_3NO_2) 8·35–7·00 ppm (m, aromatic). Found: C, 60·2; H, 3·3; N, 26·4. Calculated for $C_{32}H_{20}N_{12}Cu$: C, 60·5; H, 3·1; N, 26·45%.

3.10 Synthesis of copper tetra-3-iodophthalocyanine (X)

Copper tetra-3-aminophthalocyanine (3·0 g, 4·72 mmol), 5·2 ml conc. HCl and 5·2 ml water were mixed and cooled to −5°C. While the mixture was stirred, a solution of sodium nitrite (2·0 g in 3·0 ml water) was introduced. The mixture was then added portionwise to a solution of 4·0 g of KI in 14·0 ml HCl at room temperature. The solution was stirred for 90 min and heated subsequently to 40°C. The product was filtered, washed with water and acid-pasted. The product was dark blue in colour after the pigmentation process. ν_{max} (CCl_4) 1600 (substituted imine), 1500, 1420 (C—N stretching). δ (CCl_3NO_2) 8·40–7·00 ppm (m, aromatic). Found: C, 34·95; H, 1·5; N, 10·7; I, 46·6. Calculated for $C_{32}H_{12}N_8I_4Cu$: C, 35·6; H, 1·1; N, 10·4; I, 47·1%.

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