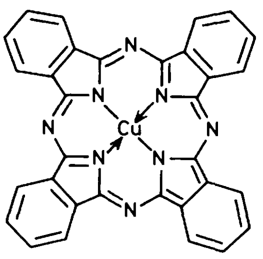
An Investigation into the Mechanism of the Phthalonitrile Route to Copper Phthalocyanines using Differential Scanning Calorimetry

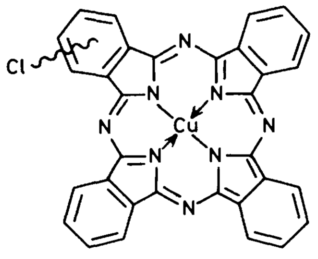
Robert M. Christie* and Derek D. Deans
Department of Technology, Scottish College of Textiles, Netherdale, Galashiels, Scotland TD1 3HF

The thermal behaviour of the reaction of phthalonitrile with a range of copper compounds has been investigated using differential scanning calorimetry with product analysis by infrared spectroscopy. Reaction with copper metal to give copper phthalocyanine (**1**) is exothermic and requires the presence of air or a small amount of a copper(II) salt. Reaction with copper(II) chloride takes place smoothly either in an air or a nitrogen atmosphere to give a copper monochlorophthalocyanine (**2**). Reaction with copper(I) chloride is air-sensitive and gives a mixture of compounds (**1**) and (**2**). A general mechanism for this industrially important series of reactions is proposed to account for the results of the thermoanalytical investigation.

Since their discovery, phthalocyanines have become one of the most extensively studied classes of compounds owing to their unique structure, their extremely high stability, and their potential for commercial exploitation.[1–5] In this last respect, copper phthalocyanine (**1**) is of particular significance being by far the most important blue pigment, finding extensive use as a colourant for 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.



(**1**)



(**2**)

One method of some commercial significance for the manufacture of copper phthalocyanine pigments involves the reaction of phthalonitrile (benzene-1,2-dicarbonitrile) with copper metal or a copper salt at elevated temperatures either in the melt phase or in a high-boiling solvent. This phthalonitrile route to phthalocyanines, reported initially by Linstead *et al.*,[6,7] has been the subject of a number of investigations[8–11] and attempts have been made to explain, mechanistically, the reaction sequence by which the phthalocyanine system is constructed from individual phthalonitrile units.[5,10] However, these earlier reports do not provide a complete explanation, failing to account, for example, for the role in the process of the various oxidation states of copper and for the observation that while reaction of phthalonitrile with copper metal gives copper phthalocyanine (**1**), reaction with copper(II) chloride gives a monochloro-substituted derivative (**2**). In this paper, we report the results of an investigation into the thermal course of the reaction of phthalonitrile with a range of copper derivatives using differential scanning calorimetry from which a clearer

Table. DSC results for the reaction of phthalonitrile with copper metal and a range of its salts in the DSC cell[a]

		DSC data		
Sample	Copper compound	Nature of reaction	Extrapolated onset temperature/°C	Peak temperature/°C
I	Copper bronze	Broad exotherm	236	283
II	CuCl	Two sharp exotherms	182, 224	194, 244
III	CuCl[b]	Sharp exotherm	188	194
IV	CuBr	Sharp exotherm	244	261
V	CuI	No reaction	—	—
VI	CuSCN	No reaction	—	—
VII	$CuCl_2 \cdot 2H_2O$	Sharp exotherm	252	260
VIII	$CuSO_4 \cdot 5H_2O$	Sharp exotherm	209	217
IX	$Cu(NO_3)_2 \cdot 3H_2O$	Sharp exotherm	[c]	134
X	$Cu(CH_3CO_2)_2 \cdot H_2O$	Sharp exotherm	204	206
XI	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$	Sharp exotherm	244	253
XII	CuF_2	Sharp exotherm	247	256

[a] Mole ratio 4:1; static air atmosphere; endothermic loss of water of crystallisation (where present) and melting of phthalonitrile (extrapolated onset temperature 140 °C, peak temperature 142 °C) were also observed. [b] Molar ratio 2:1. [c] Not measurable owing to a degree of overlap of the reaction exotherm with endotherms due to water loss and melting of phthalonitrile.

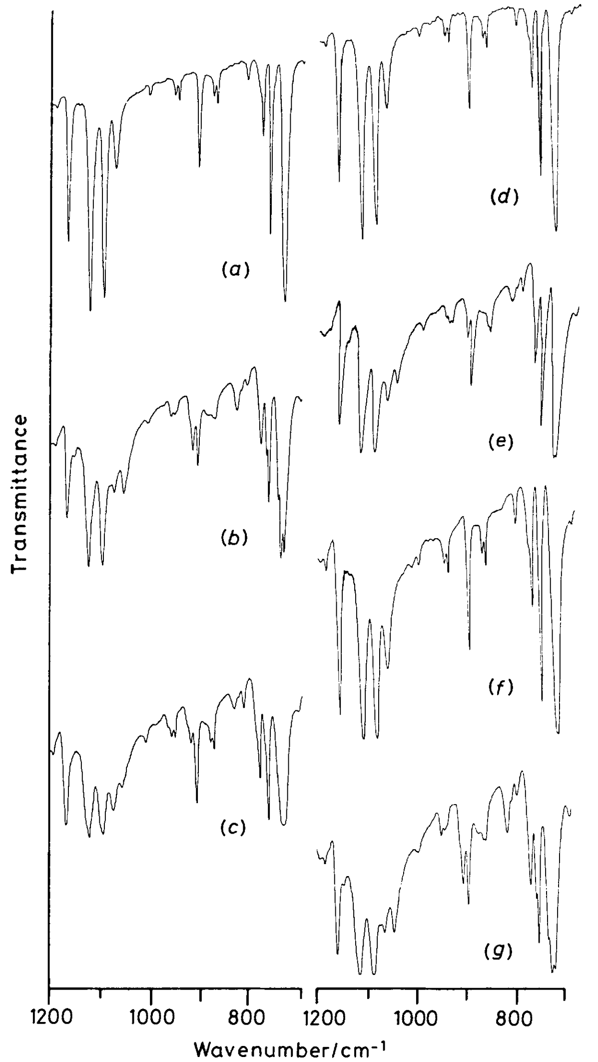


Figure 1. I.r. spectra: (*a*) copper phthalocyanine (**1**); (*b*) copper monochlorophthalocyanine (**2**); (*c*) equimolar mixture of (**1**) and (**2**); (*d*) product from the reaction of phthalonitrile with copper bronze (sample I) in DSC cell; (*e*) product from reaction of phthalonitrile with copper(I) chloride (4:1 mole ratio) (sample II) in DSC cell; (*f*) product from the reaction of phthalonitrile with copper(I) chloride (2:1 mole ratio) (sample III) in DSC cell; (*g*) product from reaction of phthalonitrile with copper(II) chloride (sample VII) in DSC cell

understanding of the nature of the reactions has emerged and a more detailed mechanism for phthalocyanine formation is proposed.

Results and Discussion

The principal traditional applications of differential scanning calorimetry (DSC) have been in the study of changes in heat capacity and enthalpy within polymeric materials as they undergo thermally induced physical or chemical transformations, and in monitoring the solid-state decomposition reactions of inorganic materials. However, the technique also offers considerable and largely unexploited potential for monitoring the thermal behaviour of some organic reactions when those reactions are carried out in the DSC cell. The method is not universally applicable, for example since DSC sample cells open to the atmosphere are generally used which presents problems when volatile solvents, reactants or products

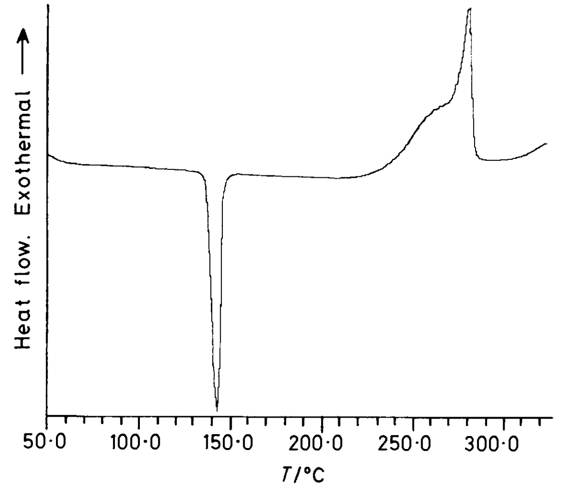


Figure 2. DSC trace for reaction of phthalonitrile with copper bronze (sample I)

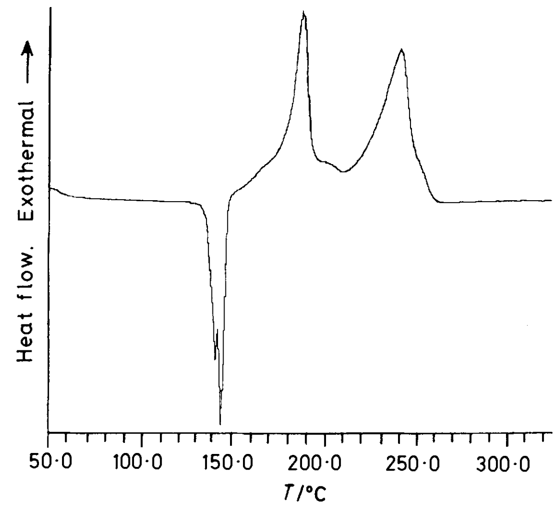


Figure 3. DSC trace for reaction of phthalonitrile with copper(I) chloride (4:1 mole ratio) (sample II)

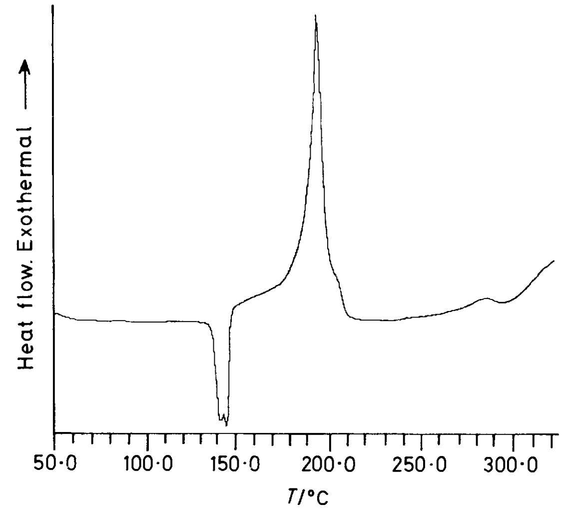


Figure 4. DSC trace for reaction of phthalonitrile with copper(I) chloride (2:1 mole ratio) (sample III)

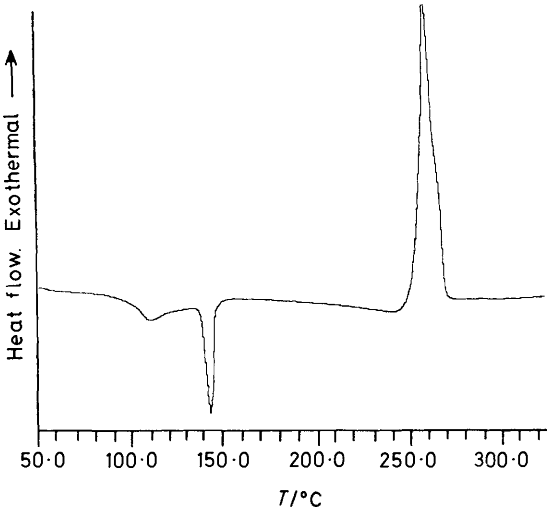


Figure 5. DSC trace for reaction of phthalonitrile with copper(II) chloride (sample VIII)

are involved. In the present study, we have found the reactions of phthalonitrile with copper and a range of its salts, which take place efficiently in the melt phase to produce thermally stable non-volatile products, to be particularly amenable to investigation by DSC and the results obtained under carefully controlled conditions have provided qualitative information of value in the elucidation of the mechanism of the reaction sequence.

The DSC data obtained from the range of reactions investigated are given in the Table. In each case, the small amount of crude product which remained in the DSC cell on completion of the run was purified by sulphuric acid pasting followed by examination using infrared spectroscopy. The i.r. spectra of purified authentic samples of copper phthalocyanine (**1**) and the chloro derivative (**2**), two of the products anticipated on the basis of prior knowledge,[6,7] were found to be extremely similar. However, in the 700—1 200 cm^{-1} region, the spectrum of compound (**2**) [Figure 1(*b*)] shows, in addition to all of the absorption bands in the spectrum of compound (**1**) [Figure 1(*a*)], three new peaks of medium intensity at 1 049, 910, and 819 cm^{-1}, and these differences are of value in providing a distinction between the two products. These absorption bands were previously reported in detailed studies of the i.r. spectra of copper phthalocyanine and its chlorinated derivatives although no conclusive assignments concerning their origin were made.[12,13]

In their early publication, Linstead *et al.*[7] report that at temperatures in excess of 200 °C, phthalonitrile and copper bronze undergo a highly exothermic reaction to form copper phthalocyanine (**1**) with the reaction stoicheiometry of equation (A).

$$4C_6H_4(CN)_2 + Cu \longrightarrow \underset{(\mathbf{1})}{C_{32}H_{16}N_8Cu} \qquad (A)$$

Attempts to carry out the reaction of phthalonitrile with copper bronze (4:1 mole ratio) in a flowing nitrogen atmosphere in the DSC cell were unsuccessful. The DSC traces obtained from numerous experiments in which the sample size and heating rate were varied systematically showed only endotherms due to the melting and vaporisation of phthalonitrile and in each case only unchanged copper metal remained in the cell. This is in agreement with a previous observation[9] that the reaction of phthalonitrile with copper in pyridine solution is inhibited by the exclusion of air. In contrast, when the DSC experiment was conducted in a static air atmosphere a broad exotherm was observed following the melting point of phthalonitrile (Figure 2). The i.r. spectrum of the product and in particular the 700—1 200 cm^{-1} region [Figure 1(*d*)] indicated that the product was copper phthalocyanine (**1**). A probable explanation for the air-sensitivity of the reaction is that oxidation of the metal to copper(II), at least in part, is required to promote copper phthalocyanine formation. Further evidence in support of this explanation was provided when it was observed that phthalonitrile reacted in a nitrogen atmosphere in the DSC cell with a copper bronze–copper(II) chloride mixture (mole ratio 4;0.95:0.05) to give compound (**1**) producing a similar DSC trace to that shown in Figure 2.

Linstead *et al.*[7] report that phthalonitrile reacts with copper(I) chloride in two stages [equations (B) and (C)] ultimately to form equimolar proportions of copper phthalocyanine (**1**) and its monochloro derivative (**2**).

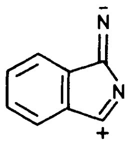
$$4C_6H_4(CN)_2 + 2CuCl \longrightarrow \underset{(\mathbf{1})}{C_{32}H_{16}N_8Cu} + CuCl_2 \qquad (B)$$

$$4C_6H_4(CN)_2 + CuCl_2 \longrightarrow \underset{(\mathbf{2})}{C_{32}H_{15}ClN_8Cu} + HCl \qquad (C)$$

In a static air atmosphere in the DSC cell phthalonitrile and copper(I) chloride (4:1 mole ratio, sample II) were indeed found to react in two distinct exothermic phases (Figure 3), the i.r. spectrum of the crude product [Figure 1(*e*)] being essentially the same as that of an authentic mixture of compounds (**1**) and (**2**) in equimolar proportions [Figure 1(*c*)]. Further, it was found that reducing the amount of phthalonitrile in the reaction mixture led to a progressive decrease in the magnitude of the second exotherm and in the intensity of the absorption bands characteristic of the monochloro derivative (**2**) in the i.r. spectrum of the product. With the reactants in a 2:1 mole ratio (sample III), the DSC trace showed only the lower-temperature exotherm (Figure 4), and the i.r. spectrum of the product [Figure 1(*f*)] indicated that it was substantially the unsubstituted copper phthalocyanine (**1**). These results, consistent with Linstead's scheme are due to an inability to form compound (**2**) [equation (C)] after the complete consumption of phthalonitrile in the first stage of the reaction [equation (B)] when the amount of phthalonitrile is restricted. Phthalonitrile and copper(I) chloride were found to react exothermically in the DSC cell in a flowing nitrogen atmosphere, but difficulties were experienced in obtaining consistent reproducible traces. This is in agreement with observations by previous workers attempting to carry out the reaction of phthalonitrile with copper(I) salts in pyridine in the absence of air.[9] We interpret this as evidence that, as in the case of copper metal, oxidation to copper(II), at least in part, is essential for the formation of the phthalocyanine.

Both copper(I) iodide and copper(I) thiocyanate failed to react with phthalonitrile in the DSC cell even in the presence of air. This result is also consistent with a phthalocyanine-formation mechanism involving copper(II), since each of these copper(I) salts is reported to be resistant to oxidation, the corresponding copper(II) salts being highly unstable.[14]

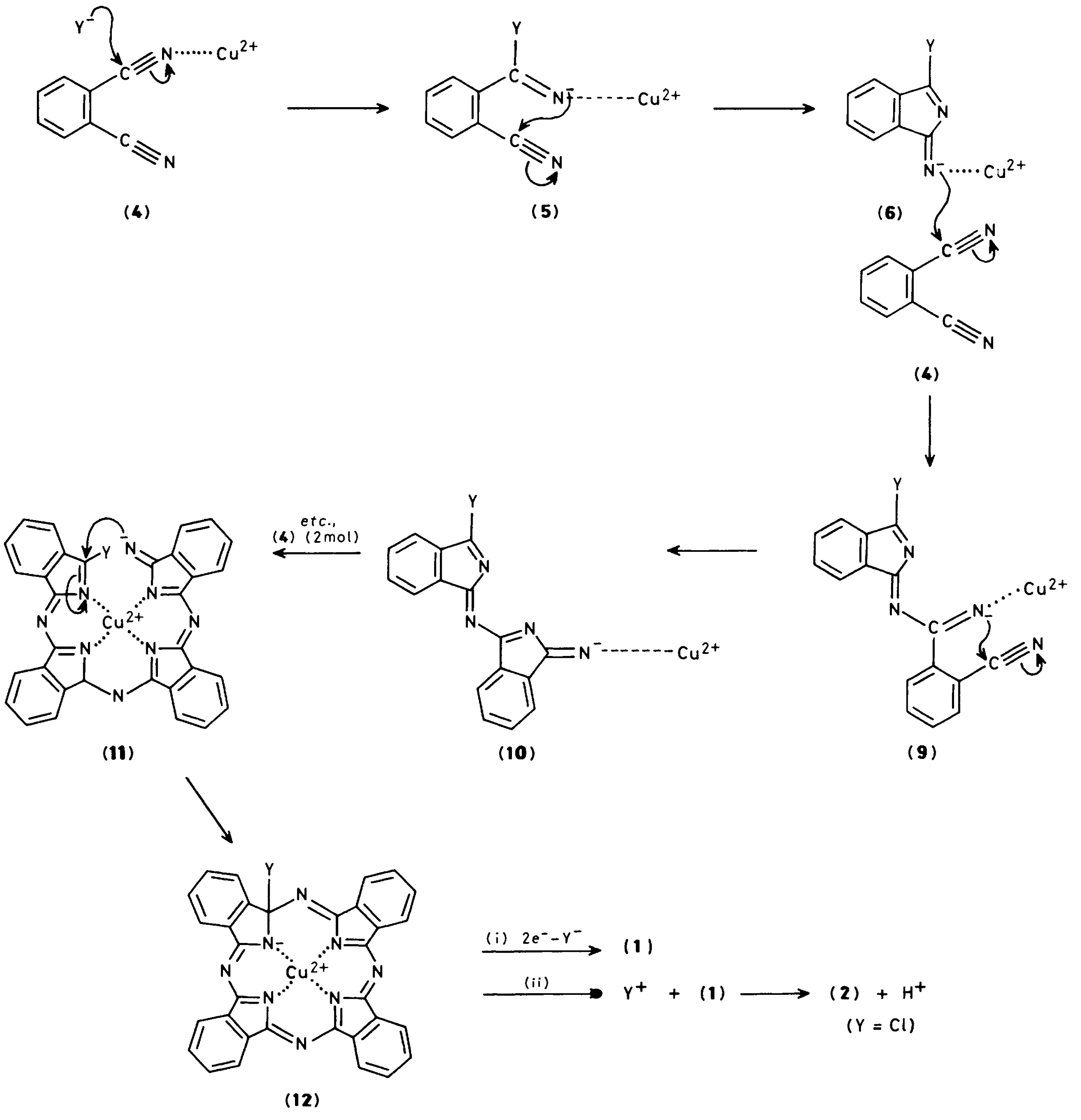
The DSC trace obtained for reaction of phthalonitrile with copper(II) chloride dihydrate (sample VII) in a static air atmosphere is shown in Figure 5. After initial endotherms due to loss of water of crystallisation from the copper salt and the melting of phthalonitrile, chemical reaction is shown as a pronounced sharp exotherm. The i.r. spectrum of the blue product [Figure 1(*g*)] is consistent with the formation of a copper monochlorophthalocyanine (**2**) [equation (C)] in agreement with the earlier observations of Linstead *et al.*[7] The position of the chloro substituent has not been unequivocally established. In this case, essentially the same DSC trace and



(3)

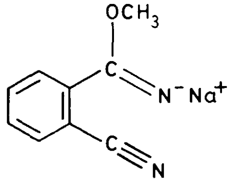
product resulted when the experiment was repeated in a flowing nitrogen atmosphere. Similar DSC traces showing a single reaction exotherm were obtained for the reaction of phthalonitrile with the sulphate, acetate, basic carbonate, and fluoride of copper(II) and with copper(I) bromide (Table 1). In each of these cases the i.r. spectra of the products were very similar to that of copper phthalocyanine (**1**), although the possibility that a small amount of ring substitution may have taken place cannot be excluded. This novel application of DSC appears to offer considerable potential in the investigation and monitoring of organic melt reactions of this type, for example in establishing optimum reaction conditions. It is of interest, for example, that reaction with phthalonitrile proceeds at significantly lower temperatures with the sulphate and acetate (Table 1) than with the other copper(II) derivatives studied. Reaction with copper(II) nitrate trihydrate (sample IX) was exceptional in showing a pronounced exotherm immediately following the melting point of phthalonitrile. The black product remaining in the DSC cell showed no trace of a copper phthalocyanine derivative and may well have resulted from degradation of the phthalonitrile by oxidation or nitration involving the nitrate ion.

In previous proposals put forward to explain mechanistically the formation of the phthalocyanine ring system from

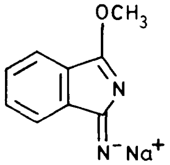


Scheme.

phthalonitrile in the presence of metal ions, the involvement of the dipolar species (**3**) is suggested.[5,10,15] In our opinion, the formation of structure (**3**) from phthalonitrile (**4**) is unlikely because of the linear arrangement of the cyano groups which means that the lone pair on the nitrogen of one cyano group is too remote from the carbon of the other for any interaction to take place in the absence of an external reagent. We now propose the mechanistic sequence shown in the Scheme to account for the range of results obtained in the DSC investigations. In the Scheme it is proposed that reaction is initiated by attack by a nucleophile (Y^-), most likely the counter-anion associated with copper but a conceivable alternative is another phthalonitrile molecule, at one of the cyano groups activated by co-ordination of the nitrogen atoms with the Cu^{2+} ion. As a result, the linear geometry changes to trigonal in structure (**5**) facilitating cyclisation to the isoindolenine intermediate (**6**). Support for this sequence is provided by Borodkin[11] who reported the isolation and characterisation of each of the sodium salts (**7**) and (**8**) from the reaction of phthalonitrile with sodium methanolate under mild conditions. It was found that both (**7**) and (**8**) were converted smoothly on heating into disodium phthalocyanine. In our proposed route to copper phthalocyanine, the Scheme suggests nucleophilic attack by intermediate (**6**) on a further molecule of phthalonitrile and following a sequence of similar reactions a tetraisoindolenine (**11**) is constructed.

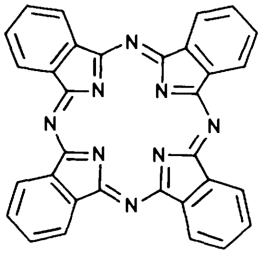


(**7**)



(**8**)

The observations that efficient reaction of phthalonitrile with copper metal and copper(I) salts requires the presence of air whereas reaction with copper(II) salts does not, and that the presence of a small amount of a copper(II) salt allows the reaction with copper metal to proceed in a nitrogen atmosphere, lead us to suggest that in all cases it is the Cu^{2+} ion which participates in phthalocyanine formation. The Scheme shows how co-ordination with the Cu^{2+} ion might play a role in retaining structure (**11**) in a conformation favourable for ring closure by intramolecular nucleophilic attack to form intermediate (**12**). Direct elimination of the original nucleophile (Y^-) from intermediate (**12**) is not favoured as this would lead to the dehydrophthalocyanine (**13**) which is generally considered as a 16 π-electron system[2] and as such is highly unstable. In the case where copper metal is the reactant we suggest that two electrons are transferred from the metal allowing elimination of Y^- to form the very stable 18 π-electron copper phthalocyanine (**1**) [route (i)]. Consequently, the copper(0) is oxidised to copper(II) as required to participate further in the reaction sequence. When copper(II) chloride is the reactant so that there is no comparable reducing agent present, we suggest that Y^+ (in this case the chloronium ion) is eliminated to form copper phthalocyanine (**1**), route (ii), the driving force for this elimination being the exceptionally high stability of compound (**1**). The eventual formation of the copper monochlorophthalocyanine (**2**) in this case is explained by a subsequent electrophilic substitution reaction involving compound (**1**) and the chloronium ion released. We suggest that when copper(I) chloride reacts, initially route (i) is followed, the source of the two electrons required being two Cu^+ ions. The result of this first phase of the reaction sequence is the formation of equimolar amounts of compound (**1**) and copper(II) chloride, the latter reacting subsequently in the second phase by route (ii) to give compound (**2**). In the case of the other copper salts which have been shown to react with phthalocyanine it is likely that the counter-anions will act as the source of the electrons essential for phthalocyanine formation, although it has not been established in the present study whether this results in the formation of electrophilic species and subsequent ring substitution of the type observed with the chlorides.



(**13**)

Experimental

Phthalonitrile was purified by recrystallisation from water. The copper salts were commercial analytical grade reagents. Authentic samples of copper phthalocyanine (**1**) and copper monochlorophthalocyanine (**2**) were prepared by the methods of Linstead *et al.*[7]

For the DSC investigation, bulk samples of mixtures of phthalonitrile with the copper salt in the appropriate mole proportions were ground intimately with a mortar and pestle. The ground material (*ca.* 10 mg) was then transferred into the standard aluminium DSC cells. DSC traces were obtained on a Mettler DSC 30 differential scanning calorimeter in the range 50—330 °C at a heating rate of 10 K min^{-1}, in either a static air or flowing nitrogen atmosphere as required. The crude products were removed from the DSC cells at the end of each run and dissolved in concentrated sulphuric acid (0.5 cm^3) at room temperature. The pigments were reprecipitated by dilution with water (10 cm^3), collected by centrifugation, washed thoroughly with water and dried at 100 °C. Infrared spectra were recorded as KBr discs with a Perkin-Elmer 599B spectrophotometer.

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