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SYNTHESIS AND CHARACTERIZATION OF 2,9,16,23-TETRA(3-PYRIDYLOXY)-PHTHALOCYANINE IN THE FORM OF ITS ZINC(II) CHELATE

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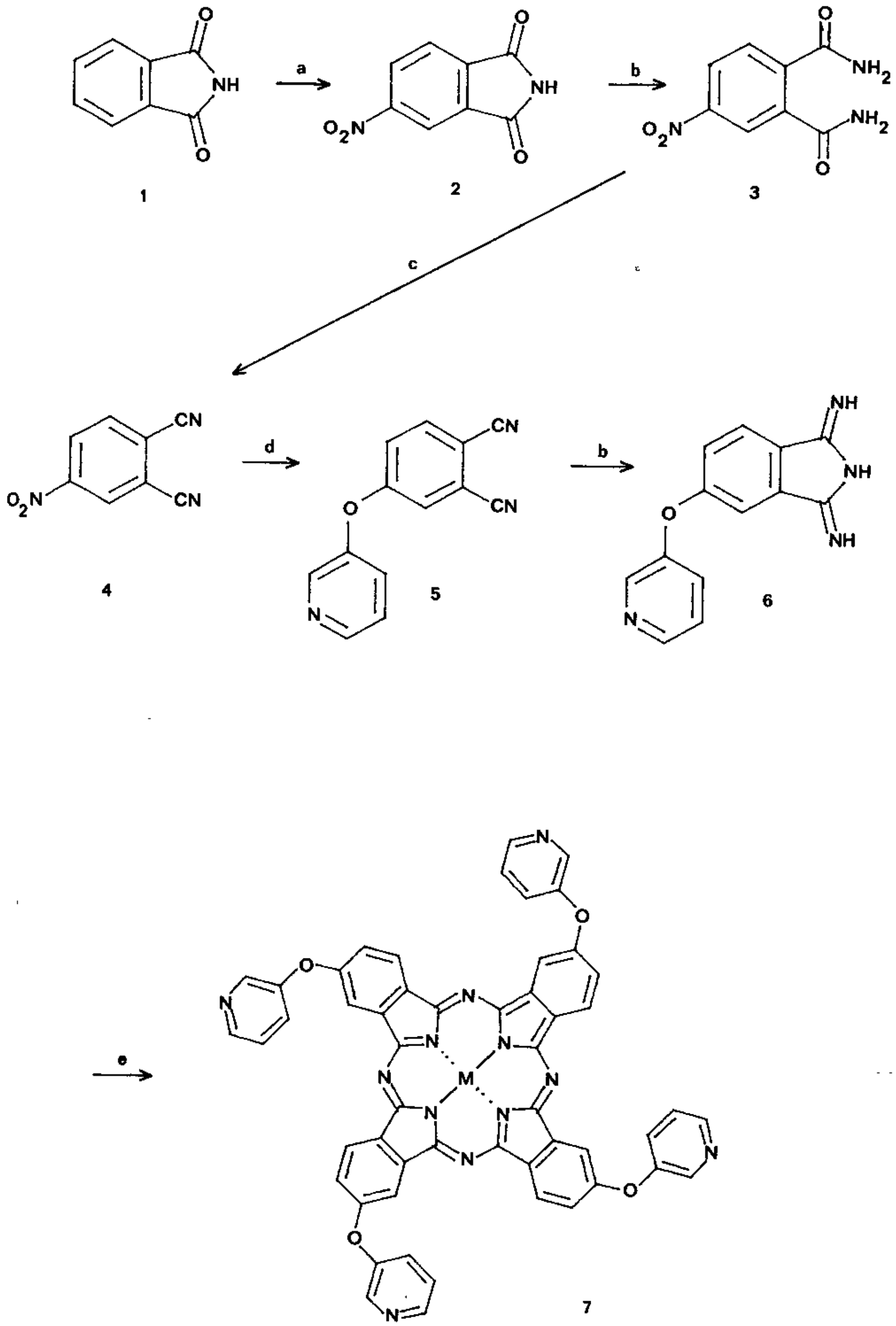
Abstract - 2,9,16,23-Tetra(3-pyridyloxy)phthalocyanine has been prepared by the reaction of lithium chloride with 5-(pyridyloxy)-1,3-diiminoisoindoline in 2-(dimethylamino)-ethanol solution followed by demetallation. The zinc chelate of the phthalocyanine has been prepared in a similar condensation reaction using zinc chloride.

The usual method for the synthesis of metallo-phthalocyanines involves heating of reaction mixtures containing phthalonitrile or phthalic acid, urea, ammonium chloride, metal salts and a catalyst such as ammonium molybdate. It has been shown that the sequence of reactions leading to the formation of metallo-phthalocyanines involves the template condensation of diiminoisoindoline which is formed in the reaction mixture.[1,2] Other methods used for the synthesis of metallo-phthalocyanines, such as treatment of phthalonitrile with metal alkoxides or the electrolysis of an ethanolic solution of phthalonitrile, have also been shown to involve intermediate compounds formed from diiminoisoindolines.[3,4] Good yields of metallo-phthalocyanine are obtained by the condensation of diiminoisoindoline in the presence of metal salts[5] and metal free phthalocyanines with substituents in the ring system have been prepared by the slow auto-condensation of diiminoisoindoline and related compounds in refluxing 2-(dimethylamino)ethanol.[6] To prepare novel phthalocyanines containing substituent groups which could degrade in severe reaction conditions it was thought advisable to utilise metal-template condensation reactions involving diiminoisoindoline containing the appropriate substituent groups. Diiminoisoindoline can be prepared by ammoniation of phthalonitrile.[1] However, substituted phthalonitriles have traditionally required arduous preparations. Recently it has been shown that nucleophilic substitution of various electron-withdrawing groups on aryl rings can be facilitated by specific activation. For instance, nitrophthalimide and 4-nitrophthalonitrile react with nucleophilic reagents to give the substituted imides and nitriles in good yield.[7] The substituent groups introduced by this reaction may be stable towards ammoniation such that reaction with ammonia provides the substituted diiminoisoindoline which may be used to produce the substituted phthalocyanines.



a) HNO_3/H_2SO_4 b) $NH_3(l)/CH_3OH$ c) $SOCl_2/DMF$ d) $C_6H_5CH_2N(CH_3)_3{}^+C_5H_4NO^-/DMSO$

e) MCl_n/dimethyaminoethanol

The solubility properties of the phthalocyanines are influenced by the nature of the peripheral groups. The range of such groups capable of effecting water solubility is small, the usual functional groups used for this purpose being sulphonic or carboxyl groups. To extend the range of substituents capable of water solubilisation of the phthalocyanine the strategies of syntheses outlined here have been used to introduce peripheral pyridyloxy groups which upon protonation are converted to the pyridinium cationic form which endows water solubility on the macrocyclic compound.The formation of phthalocyanine from the condensation reaction of substituted diiminoisoindoline could result in the formation of various isomers. In the absence of structural information the compound is tentatively assigned as 2,9,16,23-tetra(3-pyridyloxy)phthalocyanine which offers minimal hindrance by the peripheral 3-pyridyloxy groups. There is no chromatographic evidence to indicate the presence of isomers in the phthalocyanine product obtained by the synthesis outlined here.

2,9,16,23-tetra(3-pyridyloxy)phthalocyanine (tpopc) in the form of its lithium(I) or zinc(II) chelate was prepared by the sequence of the reaction scheme. Treatment of 4-nitrophthalimide with ammonia in methanol solution leads to formation of the corresponding amide. Reaction of 4-nitrophthalamide with thionyl chloride in cold N,N-dimethylformamide (DMF) affords 4-nitrophthalonitrile, which reacts with benzyltrimethylammonium pyridin-3-olate in dimethyl sulphoxide (DMSO) to give 4-(3-pyridyloxy)phthalonitrile. This latter product when reacted with ammonia in methanol solution forms 5-(3-pyridyloxy)-1,3-diiminoisoindoline.

Condensation of the substituted diiminoisoindoline in 2-(dimethylamino)ethanol containing lithium chloride leads to the formation of the dilithium form of the phthalocyanine (tpopc) which when treated with dilute hydrochloric acid followed by neutralization with ammonia gives the free base form of the phthalocyanine. The yield of phthalocyanine (tpopc) obtained by this process is not large (16%). However, in the absence of lithium chloride only vestigial quantities of phthalocyanine (tpopc) are formed from the reaction mixture. In the presence of anhydrous zinc(II) chloride the yield of phthalocyanine (tpopc) increased to about 20% in the form of its zinc(II) chelate.

The free base form of the phthalocyanine (tpopc) obtained by demetallation of dilithium tpopc is soluble in a number of organic solvents which includes DMSO, DMF and pyridine.

The zinc(II) chelate of (tpopc) is soluble in DMSO, DMF, pyridine and in water containing a little hydrochloric acid. The electronic spectrum due to an aqueous solution of zinc(II) tpopc , 0.1 M with respect to hydrochloric acid, points to the presence of extensive solute-solute interaction in the aqueous solution of the chelate, as has been found for the water soluble metallotetrasulphophthalocyanines.[8]

EXPERIMENTAL

3-Hydroxypyridine, phthalimide, and benzyltrimethylammonium methoxide were obtained from commercial sources. All solvents which included dimethyl sulphoxide were dried using the appropriate procedure, distilled and stored over molecular sieves. 2-(Dimethylamino)ethanol was distilled, and the fraction boiling at 134 °C was collected over molecular sieves. Anhydrous zinc(II) chloride was prepared by heating to about 250 °C the hydrated compounds in a stream of dried nitrogen containing dried hydrogen chloride.

The infrared spectra of the various compounds were recorded using a Jasco IRA-1 spectrophotometer, their mass spectra recorded on a V.G. Micromass 7070F mass spectrometer, their proton nuclear magnetic resonance spectra on a Bruker WH 90 spectrometer at 90 MHz, and the electronic spectra in the ultraviolet and visible light regions recorded on a Varian 635 spectrophotometer at room temperature using 1 cm glass cells. Melting points were observed with a Buchi SMP-20 apparatus. Microanalyses were carried out by the CSIRO Microanalytical Service.

Preparation of 4-nitrophthalamide (3)

4-Nitrophthalimide (2) (85 g) prepared by the method described in the literature[9] was stirred in methanol (1000 ml) cooled in a solid carbon dioxide/acetone bath. Liquid ammonia (1000 ml) was added to the cold methanol suspension and excess ammonia allowed to evaporate off. The product precipitate was filtered, washed with methanol (3 x 150 ml) and residual solvent removed by air stream at 35 °C. The yield of product was 98% (91 g). [Found: C, 45.94; H, 3.17; N, 20.15%. $C_8H_7N_3O_4$ requires C, 45.94; H, 3.38; N, 20.09%]. Ir spectrum in Nujol: ν = 3400, 3200 ($-NH_2$); 1360, 1520 ($-NO_2$); 1650 cm^{-1} (-CO).

Preparation of 4-nitrophthalonitrile (4)

A suspension of 4-nitrophthalamide (82 g) in dried DMF (200 ml) cooled to 0 °C was added slowly (over 20 min) to a solution of thionyl chloride (60 ml) in cold DMF.[10] The reaction mixture was allowed to come to room temperature and poured on to ice (3000 g) to separate the product which was filtered, dried and recrystallized from a water-DMF solution. Further recrystallization was carried out by first dissolving the product in hot ethanol (750 ml) to which was added hot water (750 ml) to give crystalline material on cooling. Yield of dried compound 56.4 g (84%); mp 144 °C [Found: C, 55.07; H, 1.73; N, 24.53%. $C_8H_3N_3O_2$ requires C, 55.50; H, 1.75; N, 24.77%]. Mass spectrum m/e 173 (65%), 127 (100%), 100 (55%). I.R. spectrum in Nujol ν = 2230 (-C≡N), 3100, 1540, 1360 cm^{-1} ($-NO_2$). ^1H nmr spectrum ($CDCl_3$) δ = 8.67 (S, 1H); 8.56 (d, J = 2.3 Hz); 8.09 (d, J = 2.3 Hz, ^1H).

Preparation of benzyltrimethylammonium 3-pyridyloxide

A methanol solution (20 ml) of 3-hydroxypyridine (5.50 g) was mixed with a 40% solution (26.2 g) of benzyltrimethylammonium methoxide in methanol. The methanol was removed from the reaction mixture by distillation at diminished pressure. The residue was heated to about 70 °C while at low pressure. The product was a viscous oil and used without further purification.

Preparation of 4-(3-pyridyloxy)phthalonitrile (5)

A dimethyl sulphoxide (25 ml) solution of 4-nitrophthalonitrile (10 g) was added to a dimethyl sulphoxide (20 ml) solution of benzyltrimethylammonium 3-pyridyloxide (15 g). The reaction mixture turned a deep red colour and after warming slightly for 10 min the solution was poured on to ice (50 g) to precipitate the product, which was washed with ice-cold water and dried (10.6 g, yield 82%). Further recrystallization from ethanol/water solution was carried out (8.2 g, yield 64%). mp 126 °C. Mass spectrum m/e 221 (78%), 193 (10%), 78 (100%). Ir spectrum (Nujol) ν 2230 (-C≡N) 1595, 1570 (aromatic ring); 1305-1210 cm^{-1} (aromatic ether).

Preparation of 5-(3-pyridyoxyl)-1,3-diiminoisoindoline (6)

Liquid ammonia (50 ml) was added to a suspension of 4-(3-pyridyloxy)phthalonitrile (8.2 g) in methanol (100 ml). The reaction mixture was heated at 100 °C in a steel autoclave for 5 h. After cooling and pressure reduction of the product mixture, the methanol was removed at diminished pressure. The extremely hygroscopic product is free of original nitrile. Yield 8.6 g, 98%. mp 90 °C (dec.). Mass spectrum m/e 238 (100%), 222 (47%). Ir spectrum (Nujol) ν = 1640 (-C=N); 1550 cm^{-1} (cyclic imine).

Preparation of zinc(II) tetra-(3-pyridyloxy)phthalocyanine (7)

5-(3-Pyridyloxy)-1,3-diiminoisoindoline (0.3 g) dissolved in 2-(dimethylamino)ethanol (20 ml) was added to a solution of zinc(II) chloride (0.05 g) in 2-(dimethylamino)ethanol (20 ml). The reaction mixture was refluxed under nitrogen for 10 min. Ethanol was added to the cooled mixture to effect a precipitation of the metallophthalocyanine which was collected by centrifugation. The green product was washed with ethanol, water and finally with ethanol. The yield of the zinc(II) chelate was 0.12 g (24%). The chelate was air dried at 70 °C. [Found: C, 63.22; H, 3.07; N, 17.38%. $ZnC_{52}H_{26}N_{12}O_4 \cdot 2H_2O$ requires: C, 63.47; H, 3.07; N, 17.08%]. Electronic spectrum pyridine λ_{max} = 678 nm (ε 1.84 x 10^5).

Preparation of the ligand tetra-(3-pyridyloxy)phthalocyanine

The dilithium(I) chelate of tetra-(3-pyridyloxy)phthalocyanine was prepared by the method outlined for the preparation of the zinc(II) chelate using 0.5 g of 5-(3-pyridyloxy)-1,3-diiminoisoindoline and 0.05 g of lithium chloride. The dilithium phthalocyanine was isolated from the product mixture after removal of 2-(dimethylamino)ethanol at diminished pressure. Treatment of the chelate with aqueous hydrochloric acid (50 ml, 0.1 M) results in dissolution and demetallation and allows separation from unreacted material. Neutralization of the solution after filtration with concentrated ammonia (specific gravity 0.88) resulted in precipitation of the free base phthalocyanine, which was washed with ethanol and air dried at 70 °C, yield 0.074 g, 16%. [Found: C, 67.58; H, 3.72; N, 18.53%. $C_{52}H_{28}N_{12}O_4.2H_2O$ requires: C, 67.82; H, 3.50; N, 18.25%]. Electronic spectrum pyridine λ_{max} = 666 nm (ϵ 1.06 x 10^5).

REFERENCES

1. J.A. Elvidge and R.P. Linstead, J. Chem. Soc., 1952, 5002
2. T.J. Hurley, M.A. Robinson and S.I. Trotz, Inorg. Chem., 1967, 6, 389.
3. P.A. Barrett, D.A. Frye and R.P. Linstead, J. Chem. Soc., 1938, 1157
4. C.H. Yang and C.-T. Chang, Inorg. Chem., 1980, 19, 3542
5. J.A. Elvidge and R.P. Linstead, J. Chem. Soc., 1955, 3536
6. J.P. Brach, S.J. Grammatica, O.A. Ossanna and L. Weinberger, J. Heterocyclic Chem., 1970, 7, 1403.
7. F.J. Williams and P.E.Donahue, J. Org. Chem., 1977, 42 (21), 3414.
8. J.A. De Bolfo, T.D. Smith, J.F. Boas and J.R. Pilbrow, J. Chem. Soc., Faraday Trans.II, 1976, 401
9. "Organic Syntheses", Coll. Vol. 2, Ed. by A.H. Blatt, John Wiley & Sons, New York, 1943, 459.
10. J.C. Thurman, Chem. Ind., 1964, 752.

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