

Synthesis of Non-Uniformly 8,9,15,16,22,23-Hexaphenyl-28H,30H-tripyrzino[5,6-b,g,l]imidazolo[4,5-q]porphyrzinato-magnesium

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ABSTRACT

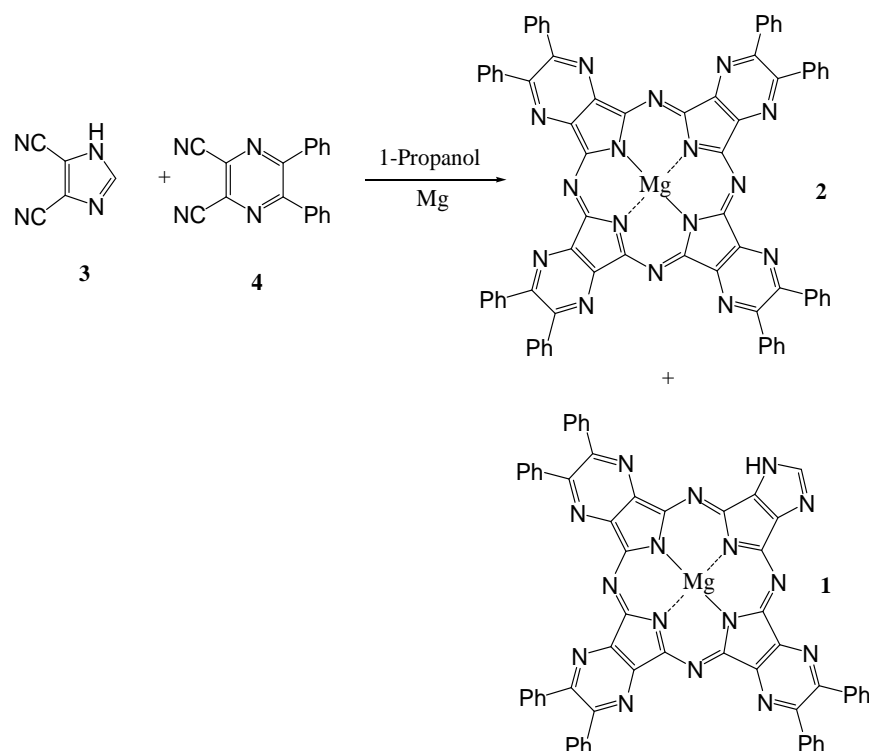
Porphyrins and their structural relatives-phthalocyanines and porphyrzines-constitute a distinct class of macrocyclic tetrapyrrolic systems with unique physico-chemical properties. Non-Uniformly 8,9,15,16,22,23-hexaphenyl-28H,30H-tripyrzino [5,6-b,g,l] imidazole [4,5-q] porphyrzinato-magnesium (an unsymmetrical porphyrzine) was prepared via mixed Linstead macrocyclization of 4,5-dicyanoimidazole and 2,3-dicyano-5,6-diphenylpyrazine. The structure of this material has been determined based on mass, FT-IR, UV-Vis and ¹H NMR spectra and elemental analysis.

Key words: Uniformly phthalocyanine, Imidazole, Porphyrzine, Dicyanopyrazine, Diaminomaleonitrile.

INTRODUCTION

Tetrapyrrolic macrocycles are widely used as pigments in textiles, polymers and paints. They are also used in photodynamic tumor therapy (PDT), gas sensing devices and organic semiconductors [1]. In recent years, research has been retargeted for application in materials as liquid crystals, Langmuir-Blodgett films, molecular semiconductors, oxidant and reductant [2]. Phthalocyanines can be synthesized such that substituents on three of the benzenoid rings are the same in terms of type and location but differ from these on the fourth. Depending upon the substituents, these so-called 3:1 Pcs can exhibit different properties [3].

There are several synthetic methods for preparing 3:1 porphyrzines. Perhaps the most common method is a mixed cyclization of two differently substituted phthalonitrile or diiminoisindoline precursors [4]. Herein, we report our studies toward the synthesis and properties of the above mentioned porphyrzine (1) by a mixed condensation approach.



Scheme 1

MATERIALS AND METHODS

Materials and instruments

Solvent and chemicals: solvents (1-propanol, absolute ethanol, methanol, CH_3COOH , pyridine and acetone) and reagents (diaminomaleonitrile, Mg powder, benzil, p-toluenesulfonic acid and 4,5-dicyanoimidazole) were pure chemicals (Merck). Chemical physical measurements: FT-IR spectra were taken with a SHIMADZU 8400S spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$ by KBr pellets. UV-Vis solution spectra were taken with a Cary 100 spectrophotometer. Mass spectroscopy was taken with a Finnigan. Mat 8430 with source power 70 eV (EI). Elemental analyses were carried out with a Thermo Finnigan (FLASH 1112 SERIES EA) CHNS-O analyzer.

Synthesis of 2,3-dicyano-5,6-diphenylpyrazine (4):

This material was prepared from diaminomaleonitrile (2.16 g, 20 mmol) and benzil (4.29 g, 20 mmol) in absolute ethanol (30 ml) in the presence of a small amount of p-toluenesulfonic acid following the procedure reported in the literature [7]. m.p. = $147\text{ }^\circ\text{C}$. IR (KBr): $3066, 2233, 1595, 1582, 1512, 1446, 1369, 1317, 1278, 1230, 1201, 1128, 1072, 1024, 935, 845, 769, 742, 573, 532$ and 495 cm^{-1} .

Synthesis of 8,9,15,16,22,23-hexaphenyl-28H,30H-tripyrzino [5,6-b,g,l] imidazolo [4,5-q] porphyrazinato magnesium (1):

Magnesium powder was refluxed overnight in 30 ml of dry propanol with the addition of a few crystals of I_2 . To this refluxing mixture, 2,3-dicyano-5,6-diphenylpyrazine (0.6 g, 2.12 mmol) and 4,5-dicyanoimidazole (0.05 g, 0.42 mmol) were added. After 2 hours, a dark blue suspension was obtained. After cooling to room temperature, propanol was evaporated under reduced pressure and the solid material was suspended in 50% aqueous acetic acid and stirred for

2 hours to dissolve the residual unchanged magnesium propylate. The resulting drak blue solid separated by filtration, washed with water to neutrality. Methanol and acetone were used in a soxhlet extractor to separate impurities from solid material. The product was then dried to constant weight in a vacuum dessicator over KOH pellets. Yield 0.19 g (29%). This porphyrazine was only slightly soluble in DMF, DMSO and pyridine. Anal. Calcd. for (C₅₉ H₃₂ N₁₆ Mg): C: 71.63, N: 22.65, H: 3.26. Found: C: 71.53, N: 22.75, H: 3.28. IR (KBr): 3417(NH, Imidazole), 3222, 1539, 729(NH, Pz) and 1656 (C=N, C=C). UV-vis (λ_{\max}) (pyridine): 357, 638, 672 nm. Mass (m/z) :636 , 580 , 376 , 315 , 276 , 272 , 257 , 103 , 76. ¹H-NMR (DMSO-d₆): 12.60 (s, 1H, NH), 8.20 (s,1H, CH), 7.50 (d, 18H, CH), 7.42 (t, 12H, CH).

RESULTS AND DISCUSSION

Statistical considerations predict that two dinitrile precursors A and B, if of the same reactivity, when reacted together in the ratio 3:1 will give a mixture of symmetric Pz (AAAA), the desired unsymmetric 3:1 Pz (AAAB) and other cross-condensation products in the following percentages: AAAA 33%; AAAB 44%; other Pz products 23% [3]. Higher ratios of A:B lower the amount of unwanted cross-condensation products.

We found that the mixed macrocyclization of 4,5-dicyanoimidazole (**3**) with a 5-fold excess of 2,3-dicyano-5,6-diphenylpyrazine (**4**) in the presence of magnesium gave the title porphyrazine **1** in 30% yield. Higher ratios of 4:3 led to the formation of symmetric tetrapyrazinoporphyrazinato magnesium (**2**) and very small amount of compound **1**. In this case the presence of small amount of compound **1** was identified by thin layer chromatography (TLC) comparison of the reaction mixture with the pure compound **1** (on silica gel using THF as eluant). It should be noted that the synthesis of compound **2** has already been reported in the literature [5, 6].

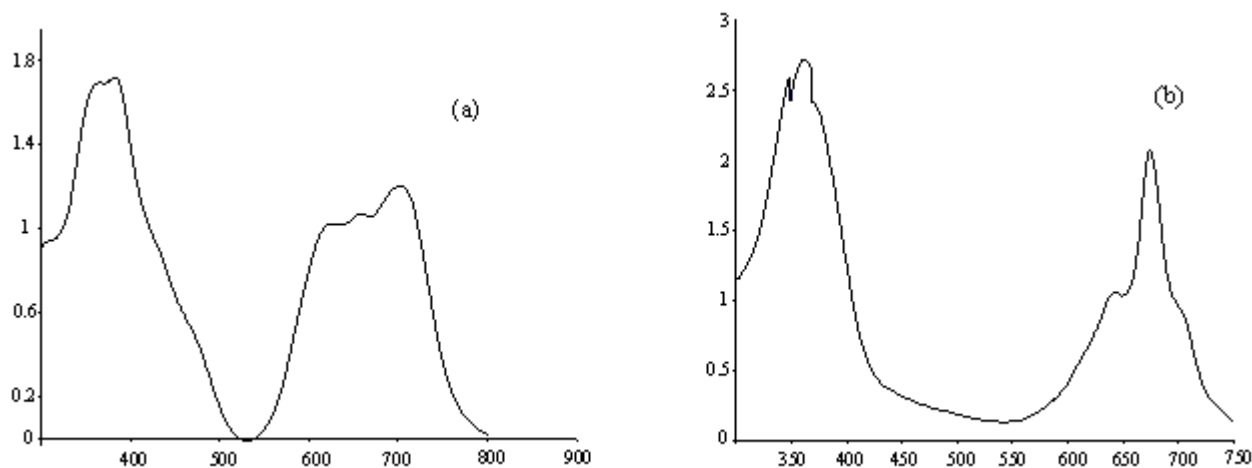


Figure 1. UV-Vis spectra of (a) compound 1 and (b) compound 2

The UV-Vis spectra of compounds **1** and **2** were shown in Figure 1. The UV-Vis spectrum of non-uniformly tripyrazinoimidazoloporphyrazine in pyridine showed the split Q-band at 638 and 672 nm and Soret band at 357 nm.

Comparison of λ_{\max} data with those for the split Q-band observed for pyrazinoporphyrazine, $\lambda_{\max} = 652$ and 698 nm and Soret band $\lambda_{\max} = 376$ nm, indicates that the replacement of one of the pyrazine rings by an imidazole ring gives rise to a hypsochromic shift.

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