



SYNTHESIS AND CHARACTERIZATION OF OCTAKIS[(2-PROPYLOXY-2-OXO-1-ETHYL)THIO]-21H, 23H-PORPHYRAZINE FROM 1,2-DICYANO-1,2-THIOETHYLENE

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Keywords: octakis[(2-propyloxy-2-oxo-1-ethylthio)-21H,23H-porphyrazine, 1,2-dicyano-1,2-thioethylene, sodium cis-1,2-dicyano-1,2-ethylenedithiolate, magnesium propoxide; 1,2-dicyano-1,2-bis(2-ethoxy-2-oxo-1-ethylthio)ethylene

The 1,2-dicyano-1,2-bis(2-ethoxy-2-oxo-1-ethylthio)ethylene has been prepared from sodium cis-1,2-dicyano-1,2-ethylenedithiolate (NaMNT) and ethyl chloroacetate by treatment with sodium iodide in dry acetone. 2,3,7,8,12,13,17,18-octakis[(2-propyloxy-2-oxo-1-ethylthio)-21H,23H-porphyrazine was obtained from 1,2-dicyano-1,2-bis(2-ethoxy-2-oxo-1-ethylthio)ethylene in magnesium propoxide (PrOMg) and dry propanol. All compounds have been fully characterized by spectroscopic data.

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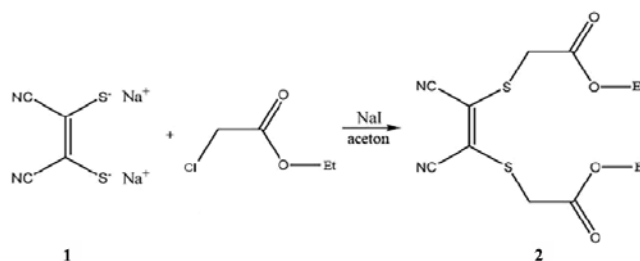
Introduction

Tetrapyrrolic macrocycles are widely used as pigments in textiles, polymers liquid crystal and paints.¹⁻³ The name porphyrazine or in other words meso-tetraaza-substituted porphyrin includes a wide class of macrocyclic porphyrin analogues or heteroanalogues.⁴⁻⁵ In the all cases the Lindsey method was used.⁶⁻⁹ Various methods such as, the organic dye photosensitization of TiO₂,^{1,6} peripherally bulky annulations of porphyrazine derivatives⁷⁻⁹ and preparation of annulated binuclear phthalocyanines¹⁰ have been developed. The modified porphyrazines possess an intensive absorption in the blue-green region of the solar spectrum; which can practically be applied in diverse areas as, photodynamic therapy (PDT), degradation of pollutants, photosensitizers, and anticancer therapy.¹¹⁻¹⁷ Diphtalocyanine complexes have also gained attention due to their rich redox chemistry and especial π -electron systems. For example, lutetium diphtalocyanine complexes show photochemical behaviors six orders higher than their monomeric counterpart.¹³

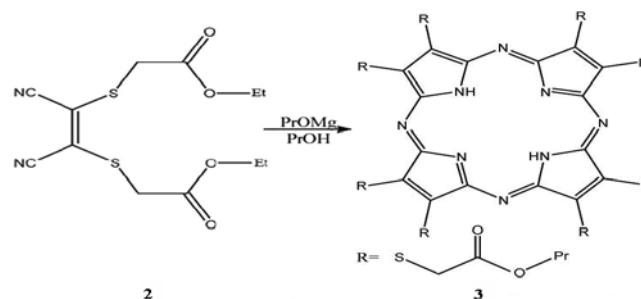
Result and Discussion

1,2-dicyano-1,2-bis(2-ethoxy-2-oxo-1-ethylthio)ethylene (2) was prepared in high yield by reaction of the sodium cis-1,2-dicyano-1,2-ethylenedithiolate (NaMNT) (1) with ethyl chloroacetate with nitrogen atmosphere in presence of a catalytic sodium iodide in dry acetone.¹¹⁻¹⁵

It was fully characterized and the spectroscopic data obtained were in agreement with those previously reported.



The microanalysis results were satisfactory and the low resolution mass spectrum gave a molecular ion peak at m/z 314[M+1]⁺. In the ¹³C NMR spectrum there were six peaks as expected, with the carbonyl at 169.4 ppm, (-CN) at 122.4 ppm, (C=C) at 111.2 ppm, (O-CH₂) at 59.9 ppm, (S-CH₂) at 40.4 ppm, and (-CH₃) at 26.0 ppm. The presences of (C-H str) were also confirmed by band at 3000 cm⁻¹, (-CN) at 2200 cm⁻¹, (C=O) at 1730 cm⁻¹, (C=C) at 1510 cm⁻¹, (-CH₂ and -CH₃ ben) at 1450 cm⁻¹ and 1375 cm⁻¹ in the infrared spectrum. 1,2-Dicyano-1,2-bis(2-ethoxy-2-oxo-1-ethylthio)ethylene (2) was then cyclised to 2,3,7,8,12,13,17,18-octakis[(2-propyloxy-2-oxo-1-ethylthio)-21H, 23H-porphyrazine (3) in 24 % yield by treatment with PrOMg in dry propanol.



Magnesium propoxide (PrOMg) has been prepared from magnesium turnings and iodine were placed in dry propanol and heated under reflux in nitrogen atmosphere overnight.

The elemental analysis and mass spectroscopy results obtained on this compound (3) were satisfactory. The ¹H

NMR spectrum showed the presence of 0.97 ppm (t, 24H, CH₃), 1.23 ppm (m, 16H, -CH₂-CH₃), 2.79 ppm (t, 16H, COO-CH₂), 3.21 ppm (s, 16H, S-CH₂). The presences of (N-H) stretching were also confirmed by band at 3400 cm⁻¹, (-CH, str) at 2960 cm⁻¹, (C=O) at 1720 cm⁻¹, (-CH₂ and -CH₃, ben) at 1480 cm⁻¹ and 1390 cm⁻¹, (C-N, str) at 1240 cm⁻¹ in the infrared spectrum. The UV-Vis spectrum showed the presence of 630 nm S-Bond and 320 nm Q-Bond.⁸⁻¹⁰

Experimental

All solvents purified and dried using established procedures. The ¹H NMR spectra were recorded on Hitachi-Perkin-Elmer R24B (60 MHz) or Bruker XL 500 (500 MHz) instruments (with *J*-values given in Hz), ¹³C NMR spectra (with DEPT 135) either on a Bruker WP 80 or XL300 instrument, and IR spectra on a Shimadzu IR-470 spectrophotometer. Mass spectra were recorded on a Kratos Concept instrument. The melting points were measured on an electrothermal digital melting point apparatus and are uncorrected.

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