

Template Assisted Cyclotetramerisations of 1,2,5-Thiadiazole-3,4-dicarbonitrile

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1,2,5-Thiadiazole-3,4-dicarbonitrile **1** reacts with copper powder in a closed vessel and in an inert atmosphere to form the corresponding copper porphyrazine **2a** in fair yields. A similar reaction of **1** with magnesium powder gives about equal amounts of unchanged **1** and the triazine **3**. Low yields of the magnesium porphyrazine **2b** were obtained from reactions of **1** with magnesium alcoholates in either 1-propanol or methanol. The required oxidation of sulfur from S^{II} in **1** to S^{IV} in the porphyrazines **2**, and stereoelectronic requirements around the nitrile functions of **1**, might explain the reluctant formation of compounds **2**.

The aromatic 18 π -electron ring system of porphyrazines (tetraazaporphyrins) and their metal complexes makes these compounds unusually stable but also almost insoluble in most organic solvents. The porphyrazines are closely related to the better known phthalocyanines, which are important industrial pigments due to their excellent coloring properties and high stability. The structure of metal-free phthalocyanine was determined in 1934 by Linstead,¹ and over the following decades the chemistry of metallophthalocyanines and porphyrazines was elucidated by Linstead and coworkers. Several reviews and monographs on the chemistry and applications of these compounds have appeared more recently.^{2–6} The metallophthalocyanines constitute a highly interesting class of compounds, with a wide range of applications, e.g., as industrial dyes, in photoreceptors for imaging,⁷ as gas sensors,⁸ catalysts,⁹ and as pharmaceuticals in cancer therapy.¹⁰ In the native form these complexes are electrical insulators, but when partially oxidized, for instance with iodine, the conductivity can be increased 12–14 orders of magnitude, into the metallic range.^{5,11}

In the solid state the planar aromatic macrocycles are stacked in a parallel fashion; within each stack short inter-ring distances enable strong π – π interactions to occur along the stack. This arrangement, combined with a partially oxidized state of the molecular array, facilitates electron transport, preferentially in the stacking direction. Consequently, the metallophthalocyanines are, in general, highly anisotropic conductors,^{5,12} and most, but not all,¹¹ show a pronounced tendency to undergo a metal–insu-

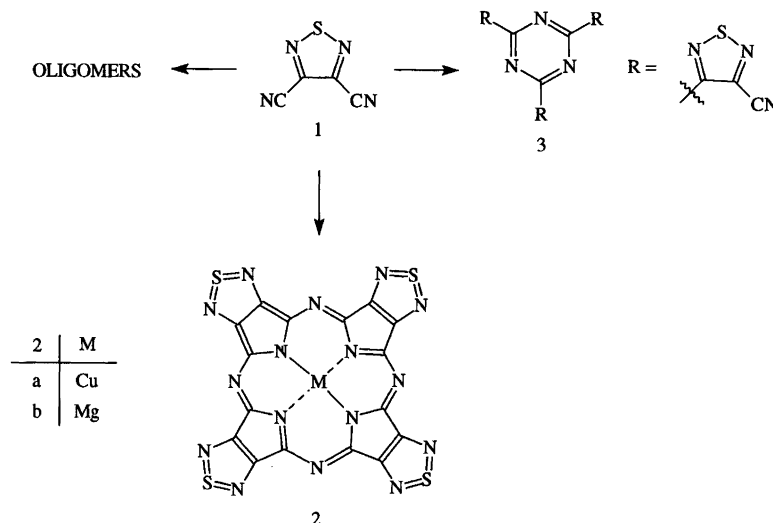
lator or metal–semiconductor transition at some temperature.

This tendency can be suppressed by promoting electron conduction in other directions. For this purpose we intend to prepare various porphyrazines and phthalocyanines with heteroatoms, in particular chalcogen atoms, in the periphery of the aromatic ligand. Chalcogens such as S or Se are known for their versatility in bonding, and are expected in the present case to advance electronic interaction between adjacent molecular stacks. A particular point of interest is the study of the effect of various peripheral substituents on intra- and inter-stack structures and their influence on the electron mobility.

This paper is a study of the reactions of 1,2,5-thiadiazole-3,4-dicarbonitrile **1** with metal templates. Expected products are metallated porphyrazines **2** as shown in Scheme 1. Previously we have reported¹³ that a bicyclic diimino imide derivative of **1** could not be obtained. Therefore, a metal-free porphyrazine **2** (M = 2H) cannot be obtained from **1** by a direct method, i.e., by heating its diimino imide in a polar solvent such as dimethylaminoethanol.¹⁴

Results and discussion

The best method we have found for the preparation of copper porphyrazine **2a**, Scheme 1, is to heat **1** with a large excess of copper powder (copper bronze) under nitrogen in a sealed ampoule at about 200 °C for 48 h.



Scheme 1. Condensations of 1,2,5-thiadiazole-3,4-dicarbonitrile.

Unchanged **1** and triazine **3**¹³ are removed from the crude reaction mixture by repeated extractions with dichloromethane. Microanalysis of the insoluble material showed the presence of copper in addition to **2a**. The excess of copper was removed with aqueous ammonium hydroxide, and **2a**·H₂O was obtained as a blue powder after drying (Experiment A1). Both microanalysis and MS data were in accord with the structure of compound **2a**. Owing to the very low volatility of the compound, flash evaporation using DEI (desorption electron ionisation) was found necessary to obtain a sufficient amount of undecomposed sample in the gas phase for MS analysis. Attempts to use desorption methods such as FD and SIMS or FAB were unsuccessful. The mass spectrum showed strong molecular ion peaks with the correct isotope distribution. Characteristic infrared absorptions were found at 1535, 1272, 1108 and 688 cm⁻¹. UV-VIS spectroscopy of 0.005 M solutions of **2a** in pyridine gave expected values of absorptions and extinction coefficients; $\lambda_{\max} = 640$ nm, $\epsilon = 75000$ M⁻¹ cm⁻¹. The pyridine solutions of **2a** were kept for several days, and slow decomposition of **2a** was observed. The product which contained excess copper, lost 75% of the absorption at 640 nm in 7 days, whereas pure **2a**, after removal of excess copper, had lost only 23% of the chromophore after 10 days. Thus, it appears that copper assists the decomposition of **2a** in pyridine. Removal of excess copper from the initial product is a slow process which requires about 2 × 24 h. The formation of **2a** requires a molar ratio of 4:1 between **1** and copper. However, we found that increasing the relative amount of copper in the reaction mixture led to increased yields of **2a**. Thus, a molar ratio of 2:1 between **1** and copper gave 16% of **2a** (Experiment A1) and a ratio of 1:1 gave 39% of **2a** (Experiment A2).

Other work-up methods, for instance reprecipitation from sulfuric acid or extraction with hot pyridine, led to extensive decomposition of **2a**.

Compound **2a** was also prepared in reactions of **1** with anhydrous copper acetate and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), a strong nitrogen base first used in the preparation of phthalocyanines by Tomoda and coworkers.¹⁵ The product which remained after extractions with organic solvents and dilute hydrochloric acid, contained about 27% of **2a** as calculated from the extinction coefficient at 640 nm. A pyridine solution of this product showed no loss of the chromophore after 6 weeks. A sample of this product was heated to about 500°C at 10⁻⁵ mmHg. Extensive decomposition occurred, but a small amount (5%) of a blue powder was isolated in addition to substantial amounts of sulfur and copper. Microanalysis of this blue powder was not satisfactory, the content of copper and carbon was somewhat high, whereas the nitrogen and sulfur content was lower than calculated for **2a**. The presence of some free copper was indicated since a pyridine solution of the solid showed extensive decomposition of the chromophore after two weeks.

The magnesium porphyrazine **2b** was obtained in low yields (3%) from a reaction of **1** with magnesium propanoate in 1-propanol. Microanalysis indicated that a solvate of **2b** was obtained, and this is in accordance with earlier findings by Linstead and coworkers.¹⁶ These workers found that magnesium phthalocyanine formed a dihydrate since a planar arrangement around magnesium seems to be unstable. The mass spectrum of **2b** showed the expected molecular ion peaks with the correct isotope distribution. The UV-VIS absorption at 645 nm ($\epsilon = 71600$) confirmed the presence of the expected chromophore, and the infrared absorptions were almost the same as observed for **2a**.

Low yields of **2b** and unidentified compounds with shorter chromophores ($\lambda_{\max} = 464-494$ nm) were obtained from reactions of **1** with magnesium alcoholates, or with anhydrous magnesium acetate and DBN. A

reaction of **1** with magnesium powder in a sealed ampoule yielded unchanged **1** (45%) and **3** (40%).

Conclusions

The three competing reaction paths: cyclotetramerisation, linear condensation and formation of triazine, are possible for **1** and other aromatic vicinal dinitriles. However, a good template like copper usually makes cyclotetramerisation the preferred reaction for most such aromatic dinitriles. The reluctance of compound **1** to form compounds **2** might be explained both by the required oxidation of sulfur from S^{II} in **1** to S^{IV} in **2**, and the stereoelectronic requirements around the nitrile functions of **1**.¹³ Further studies of these and related compounds are in progress.

Experimental

General. Mass spectra were obtained on a VG ProSpec-3000-Q mass spectrometer from Fisons Instruments, England. The samples were flash evaporated using the DCI/DEI probe, and ionised by electron ionization (EI). IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Jeol EX400 NMR spectrometer, ¹³C spectra were obtained at 100.40 MHz, ¹H spectra at 399.65 MHz. Tetramethylsilane (TMS) was used as the internal standard. UV-VIS spectra were obtained on a Perkin Elmer 522 UV-VIS spectrophotometer. Microanalyses were performed by *Analytische Laboratorien*, D-51647 Gummersbach, Germany. Melting points were obtained on a Büchi 530 melting point apparatus and are uncorrected. Merck Kieselgel 60F 254 was used for TLC and Merck silica 63–200 µm was used for column chromatography. Copper powder (copper bronze), 99% was obtained from Aldrich, and magnesium powder, 325 mesh was obtained from Johnson Matthey Alfa Products. Magnesium acetate·4H₂O (Fluka) and copper(II) acetate·H₂O (Riedel de Haen) were heated under reflux with acetic anhydride, filtered, washed with anhydrous diethyl ether and dried at 1 mmHg, 30°C. The alcohols were dried by appropriate methods and kept over molecular sieves 3 or 4 Å. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Aldrich, and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) from Janssen. 1,2,5-Thiadiazole-3,4-dicarbonitrile, **1**, was prepared by reported methods.^{13,17}

{25H,27H-Tetrakis[1,2,5]thiadiazolo[3,4-b:3',4'-g:3'',4''-l:3''',4'''-q]porphyrizin-2-S^{IV}-ato(2-)-N²⁵,N²⁶,N²⁷,N²⁸}copper, **2a**. **Method A.** A mixture of copper powder and **1** was transferred to a long-stem glass ampoule which contained a Teflon-coated magnetic stirring bar. The ampoule was degassed and filled with nitrogen three times, sealed and placed in a silicon oil bath on a hot plate with a magnetic stirrer. The reaction mixture was heated with stirring, the

ampoule was then cleaned, broken, and the contents heated under reflux with dichloromethane (3 ×). The combined organic extracts were concentrated, chromatographed on silica gel with dichloromethane to give **1** and 2,4,6-tris(4-cyano-1,2,5-thiadiazol-3-yl)-1,3,5-triazine,¹³ **3** eluted in that order. Further purification of the dichloromethane-insoluble material varied and is described separately for each experiment.

Experiment A1. Copper powder (0.64 g, 10 mmol) and **1** (2.7 g, 20 mmol) were heated at 195–200°C for 48 h. The dichloromethane extracts (3 × 70 ml) yielded 0.1 g (4%) of **1**, m.p. 48–50°C, and 1.90 g (70%) of **3**, m.p. 270°C (decomp.), lit¹³ > 290°C. IR (KBr): 1532 (vs) cm⁻¹. The blue-purple powder (1.2 g), which was insoluble in dichloromethane, was slightly soluble in pyridine, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-methylpyrrolidone and tetramethylurea, but insoluble in other common organic solvents. MS [*m/z* (% rel. int.)]: 612 (1.2, *M* + 5), 611 (7.0, *M* + 4), 610 (9.2, *M* + 3), 609 (30.5, *M* + 2), 608 (13.4, *M* + 1), 607 (45.8, *M*), 575 (6.3), 408 (47.7), 382 (31.7), 324 (22.6), 298 (12.3), 272 (12.6), 199 (12.4), 168 (11.0), 162 (14.7), 136 (67.5). Isotope distribution, calc. for C₁₆N₁₆S₄Cu [*m/z* (% rel. int.)]: 607 (100, *M*), 608 (26.89, *M* + 1), 609 (65.79, *M* + 2), 610 (16.91, *M* + 3), 611 (11.32, *M* + 4), 612 (2.56, *M* + 5). UV [abs. pyridine (ε)]: 640 (57900) nm. UV [abs. pyridine (ε)] after 7 days: 642 (14300) nm. Anal. Found: C 25.55; H 0.18; N 29.66; S 16.76; Cu 27.90. Calc. for C₁₆N₁₆S₄Cu: C 31.60; N 36.86; S 21.09; Cu 10.45. Calc. for C₁₆N₁₆S₄Cu_{3.3}: C 25.48; N 29.71; S 17.00; Cu 27.80.

A sample (0.10 g) of this product was stirred at ambient temperature with ammonium hydroxide (25%, 50 ml) for 23 h. Undissolved material was separated by centrifugation and was stirred at ambient temperature for 19 h with ammonium hydroxide (25%, 10 ml). Undissolved material was washed with water (2 × 10 ml) and acetone (5 ml) and was dried at 0.1 mmHg and 100°C. Yield of **2a**, 40 mg, m.p. > 300°C. Total yield of **2a**, 0.48 g (16%). Anal. Found: C 30.73; H 0.35; N 35.80; S 20.24; Cu 10.20. Calc. for C₁₆N₁₆S₄Cu·H₂O: C 30.76; H 0.32; N 35.76; S 20.46; Cu 10.14. IR (KBr): 1535 (s), 1489 (w), 1272 (s), 1108 (s), 879, 829, 767, 735 (s), 688 (s), 624, 513 (s) cm⁻¹. UV [abs. pyridine (ε)]: 365 (12300), 500 (2800), 580 (13300), 614 (19900), 640 (75000) nm. UV [abs. pyridine (ε)] after 10 days: 365 (13300), 500 (2800), 580 (9500), 614 (15200), 640 (57900) nm.

Experiment A2. Copper powder (0.95 g, 15 mmol) and **1** (2.04 g, 15 mmol) were heated at 175–180°C for 44 h. The dichloromethane extracts (3 × 100 ml) yielded 0.20 g (10%) of **1** and 0.80 g (39%) of **3**. The purple-blue powder, 1.72 g, insoluble in dichloromethane, was stirred with ammonium hydroxide (25%, 2 × 100 ml) for 2 × 1 h at ambient temperature, washed with water and dried at 0.1 mmHg and 100°C. Yield, 1.42 g, m.p. > 300°C. IR (KBr): identical with that of **2a** obtained in Experiment A1. UV [abs. pyridine (ε)]: 330 (22000), 366 (14420),

582 (7590), 614 (12140), 640 (44000) nm. Anal. Found: C 18.27; H 0.11; N 21.53; S 11.97; Cu 47.90.

A sample (0.40 g) of this product was stirred with ammonium hydroxide (25%, 2 × 100 ml) for 2 × 24 h. The product was washed with water and dried. UV [abs. pyridine (ϵ): 365 (12300), 500 (2800), 580 (13300), 614 (19900), 640 (75000) nm. Calculated yield of **2a**: 1.42 g of **2a** + 38% copper gives 0.88 g (39%) of **2a**.

Method B. Anhydrous copper(II) acetate and **1** were ground together in a mortar and transferred to a reaction flask. The flask was flushed with nitrogen for 15 min, DBU was added and the reaction mixture was stirred and heated at 160°C under nitrogen. The reaction mixture was cooled, then heated under reflux with dichloromethane (4 × 50 ml). Undissolved material was stirred with 2 M hydrochloric acid (40 ml) for 20 h, triturated with water (3 × 50 ml) and finally stirred at ambient temperature with tetrahydrofuran (3 × 50 ml) for 3 × 3 h.

Experiment B1. Copper(II) acetate (0.55 g, 3 mmol), **1** (1.36 g, 10 mmol) and DBU (1.52 g, 10 mmol) were heated for 16 h and yielded 1.70 g, m.p. > 300°C of a dark powder. UV [abs. pyridine (ϵ): 640 (20600) nm.

Sublimation at ca. 10⁻⁵ mmHg and 500°C of a sample (0.20 g) of this product yielded copper, sulfur, unidentified decomposition products and **2a** (10 mg) as a blue powder. UV [abs. pyridine (ϵ): 640 (76300) nm. UV [abs. pyridine (ϵ) after 2 weeks: 640 (26000) nm. Anal. Found: C 34.67; H 0.26; N 34.98; S 17.48; Cu 11.20. Calc. for C₁₆N₁₆S₄Cu: C 31.60; N 36.86; S 21.09; Cu 10.45.

Experiment B2. Copper(II) acetate (0.45 g, 2.5 mmol), **1** (1.36 g, 10 mmol) and DBU (0.90 g, 6 mmol) were heated for 4 h and yielded 1.5 g, m.p. > 300°C of a dark powder. IR (KBr): identical with the spectrum of the crude product obtained in Experiment B1. UV [abs. pyridine (ϵ): 640 (21000) nm.

{25H,27H-Tetrakis[1,2,5]thiadiazolo[3,4-b:3',4'-g:3'',4''-l:3''',4''''-q]porphyrizin-2-S^{IV}-ato(2-)-N²⁵,N²⁶,N²⁷,N²⁸} magnesium, **2b**. **Method C.** Magnesium turnings and an alcohol were heated under reflux, and under nitrogen where indicated, until the metal had been consumed. A solution of **1** in the same alcohol was added, and the reaction mixture was heated under reflux and under nitrogen for the indicated amount of time. The work-up procedures are described in each experiment.

Experiment C1. Magnesium (2.0 g, 82 mmol), **1** (1.0 g, 7.4 mmol) and 1-propanol (55 ml) were reacted for 18 h. The solvent was removed under reduced pressure and the residue was heated under reflux with hydrochloric acid (1.7 M, 100 ml) for 20 min. Chloroform (100 ml) was added, and a blue solid which was insoluble in the organic and the aqueous phase, was removed by centrifugation, washed with water and acetone, dried at

0.1 mmHg, 70°C for 18 h to yield 30 mg of a blue powder, m.p. > 300°C. MS [*m/z* (% rel. int.): 572 (8.7, *M* + 4), 571 (12.2, *M* + 3), 570 (41.2, *M* + 2), 569 (40.4, *M* + 1), 568 (100, *M*), 536 (7.5), 484 (2.8), 461 (2.7), 379 (12.9), 365 (14.3), 306 (21.7), 238 (12.5). IR (KBr): 3433 (w, br), 3342 (w), 3239 (w), 1634 (w), 1528 (m), 1480 (w), 1268 (s), 1091 (m), 1050 (m), 735 (w), 690 (m), 514 (m) cm⁻¹. UV [abs. pyridine (ϵ): 365 (24200), 500 (2100), 584 (8400), 618 (13700), 645 (71600) nm. UV [abs. pyridine (ϵ) after 6 weeks: 400 (38000), 540 (4200), 584 (7400), 618 (10500), 645 (47300) nm. Anal. Found: C 32.82; H 1.15; N 33.83; S 19.30. Calc. for C₁₆N₁₆S₄Mg: C 33.78; N 39.40; S 22.55; Mg 4.27. Calc. for C₁₆N₁₆S₄Mg + CH₃COCH₃ + 2H₂O: C 34.42; H 1.52; N 33.80; S 19.35; Mg 3.67. A Beilstein test for halogen was negative.

Experiment C2. Magnesium (0.38 g, 16 mmol), **1** (1.1 g, 8 mmol) and methanol (30 ml) were reacted for 68 h under nitrogen. Water (50 ml) was added, the suspension was acidified with hydrochloric acid (2 M) and extracted with dichloromethane (5 × 15 ml). A blue solid, insoluble in both phases, was removed by filtration and suspended in acetic acid (15 ml). The solid was filtered, washed with water and acetone, dried at 1 mmHg to yield 17 mg, m.p. > 300°C. IR (KBr): 3418 (m, br), 3223 (sh), 2548 (w), 1625 (w), 1527 (m), 1480 (w), 1269 (s), 1088 (m), 1050 (m), 734 (w), 688 (m), 514 (m) cm⁻¹. UV [abs. pyridine (ϵ): 365 (18200), 584 (7100), 618 (9500), 645 (45000) nm. Anal. Found: C 29.58; H 1.04; N 30.97; S 17.75; Mg 3.22. Calc. for C₁₆N₁₆S₄Mg + CH₃COOH + 6H₂O: C 29.45; H 2.20; N 30.53; S 17.47; Mg 3.31.

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