# 5,10,15,20-Tetracymantrenylporphyrin and 5,10,15-tricymantrenylcorrol

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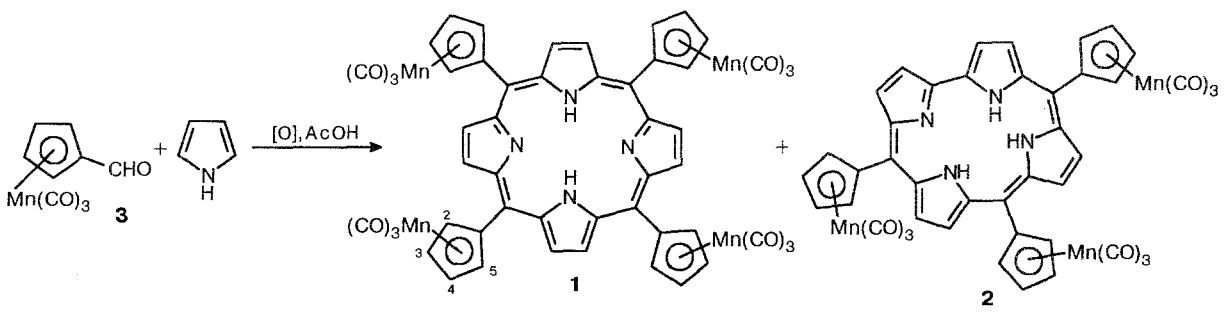
The reaction of pyrrol with cymantrenecarboxaldehyde in acetic acid results in 5,10,15,20-tetracymantrenylporphyrin (**1**) and 5,10,15-tricymantrenylcorrol (**2**). Porphyrin synthesis according to Lindsey's method only affords compound **1** in high yield. The NH-tautomerism in molecules **1** and **2** was investigated by dynamic NMR spectroscopy. It was shown that free rotation of the $(CO)_3MnC_5H_4$ fragments around the bond with the carbon atoms in the *meso*-positions of the porhpyrin macrocycle occurs.

**Key words**: porphyrin; corrol; N—H-tautomerism; cymantrene.

Recently[1] we reported on the synthesis of a new organometallic porphyrin, 5,10,15,20-tetracymantrenylporphyrin (**1**). Compound **1**, which was obtained in a 27 % yield by the condensation of cymantrenylcarboxaldehyde (**3**) with pyrrole in boiling acetic acid (Scheme 1), was initially described as an αβαβ-atropoisomer. In addition to product **1**, compound **2** was also isolated in 4 % yield. Based on the similarity of the electron absorption spectrum of compound **2** to that of porphyrin **1**, the structure of an αααβ-type atropoisomer of *meso*-tetracymantrenylporphyrin was ascribed to **2**. To increase the yield of compound **1**, we used the method proposed by Lindsey for the synthesis of sterically hindered *meso*-porphyrins,[2,3] which consists of the treatment of carboxaldehydes with pyrrole in dichloromethane in the presence of $BF_3 \cdot Et_2O$. *p*-Chloroanil was used as the oxidant. In fact, this method allowed us to increase the yield of compound **1** to 60 %. However, we could not detect compound **2** in the reaction mixture, although αααβ-atropoisomers of porphyrins are the most probable condensation products (the statistic ratio of atropoisomers αααα : αααβ : αβαβ : ααββ is usually 1 : 4 : 1 : 2).[4] Since the temperature of condensation by Lindsey's method (25 °C) is much lower than that used for the reaction in acetic acid, the formation of compound **2** in the latter case could be caused by thermal isomerization of porphyrin **1**. However, boiling a solution of **1** in toluene for 5 h did not give compound **2** or any other products.

Thus, although some physicochemical properties of compounds **1** and **2** are similar, it is likely that the latter compound is not a *meso*-tetracymantrenylporphyrin. In the previous study[1] we could not obtain the mass spectrum of compound **2** by the FAB (Xe) method in the glycerol—thioglycerol matrix. The use of plasma desorption mass-spectrometry with $^{252}Cf$ allowed us to obtain the spectra of both compound **1** and compound **2** (see Experimental). The heaviest ions in the spectrum of compound **2** have *m/z* 905 and 820, which differ by 214 au from the ions with *m/z* 1119 $[M^+ + H]$ and 1034 $[M^+ - 3CO]$ present in the spectra of porphyrin **1**. It should be noted that the ions with *m/z* 905 and 820 are also observed in the electron impact (80 eV) mass spectrum of compound **2**. The difference in the masses of the heaviest ions in the spectra of compounds **1** and **2** and the fragmentation behavior of the latter lead us to

**Scheme 1**




Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 925—927, May, 1994.

the conclusion that compound **2** is likely to have the structure of 5,10,15-tricymantrenylcorrol.

The detailed analysis of the $^1$H NMR spectrum of compound **2** obtained under the conditions of complete relaxation of nuclei, as well as the temperature dependencies of the spectra confirm that compound **2** is a corrol derivative. At 353 K in toluene the ratio of signal intensities of the β-protons in the pyrrole rings (9.3—8.5 ppm), the protons of the Cp-rings (5.7—4.6 ppm), and the NH groups (−1.3 to −2.5 ppm) is 8 : 12 : 3 rather than 8 : 16 : 2 as in the case of porphyrin **1**. The shape of the spectrum of compound **2** in the region of 4—10 ppm remains almost unchanged when the temperature is decreased to 273 K. However, in the region corresponding to NH groups, a sharp broadening of the signal to 1200 Hz occurs. A further decrease in the temperature results in changes in all regions of the $^1$H NMR spectra due to a decrease in the rate of N—H tautomerization, and at 203 K the spectrum contains three separate signals of the NH groups at δ −0.1, −4.2, and −6.9 as well as a complex system of signals of the β-protons of the pyrrole rings. The N—H tautomerization of porphyrin **1** is observed in the same temperature range: the temperature of coalescence of the signal of the β-protons of the pyrrole rings is 203 K. With further cooling this signal splits into two lines. Only one signal corresponding to NH group protons is recorded, which broadens only slightly and shifts upfield when the temperature is decreased. This indicates a symmetric structure of porphyrin **1** and probably relatively free rotation of the $(CO)_3MnC_5H_4$ moieties around the bond with the C *meso*-atoms of the macrocycle.

Thus, the synthesis of compound **2** described above is, to our knowledge, the first method for obtaining corrol derivatives by the condensation of pyrrole with aldehydes. The traditional method for the synthesis of corrols involves thermal cyclization of salts of 1,19-dibromo- or -diiodobiladienes-*a,c* to give corrols containing substituents at the β-positions of the pyrrole rings.[5—7] Compound **2** is the first example of a corrol derivative containing substituents only at the *meso*-positions of the macrocycle.[5]

## Experimental

IR spectra were recorded on a UR-20 spectrophotometer. $^1$H NMR spectra were obtained on a Bruker WP-200SY spectrometer. Electron absorption spectra and FAB-MS were recorded on a Specord-UV-VIS and a Kratos-MS-890 instruments, respectively.

**Cymantrenecarboxaldehyde (3)** was synthesized according to the reported procedure.[8]

**5,10,15,20-Tetracymantrenylporphyrin (1).** Cymantrenecarboxaldehyde **3** (1.3 g, 5.6 mmol), dry dichloromethane (120 mL), and freshly distilled pyrrole (0.4 g, 0.42 mL, 6 mmol) were placed into a three-necked flask, which was equipped with a reflux condenser, preliminarily evacuated, and filled with argon. Then $BF_3 \cdot Et_2O$ (0.038 mL, 0.3 mmol) in $CH_2Cl_2$ was added and the reaction mixture was stirred by a stream of Ar at ~20 °C for 20 h, *p*-chloroanil (0.98 g, 4 mmol) was added, and the mixture was boiled for 3.5 h. The reaction was monitored using UV spectroscopy by observing the Soret band of porphyrin (462 nm). The solvent was evaporated, and the residue was chromatographed on a column with silica gel (benzene—$Et_3N$ (100 : 1) as the eluent) to give 0.935 g (60 %) of porphyrin **1**. The yield of the product after double chromatographic purification was 0.583 g (37.4 %).

**5,10,15,20-Tetracymantrenylporphyrin (1) and 5,10,15-tricymantrenylcorrol (2).** Freshly distilled pyrrole (0.7 mL, 10.1 mmol) was added to a solution of cymantrenecarboxaldehyde **3** (2 g, 8.62 mmol) in glacial acetic acid (75 mL), and the mixture was boiled for 4 h with stirring by a stream of air. The reaction mixture was cooled, the precipitate was filtered off, and the filtrate was concentrated to 10 mL and neutralized with a solution of $Na_2CO_3$. The reaction products were extracted with $CHCl_3$. The extracts were concentrated, the residue was combined with the precipitate on a filter and chromatographed on a column with $Al_2O_3$ using succesively hexane, benzene, and chloroform as eluents. The fractions isolated with $R_f$ 0.7 and 0.3 (TLC, Alufol—$Al_2O_3$, chloroform) are compounds **1** and **2**, respectively. The solvent was evaporated to give 0.65 g (27 %) of compound **1** and 0.09 g (4 %) of compound **2**.

**Compound 1.** Found (%): C, 59.37; H, 4.71; N, 4.48; Mn, 15.92; Cl, 1.66. $C_{52}H_{26}N_4O_{12}Mn_4 \cdot 0.5CH_3CN \times \times 0.2CHCl_3 \cdot 2.5C_6H_{14}$*. Calculated (%): C, 59.42; H, 4.59; N, 4.57; Mn, 15.94; Cl, 1.54. UV ($CHCl_3$), $\lambda_{max}$/nm (log ε): 462 (4.88), 559 (3.80), 593 (3.92), 625 (3.77), 689 (3.40); ($CHCl_3$—$CF_3COOH$), $\lambda_{max}$/nm: 453, 490, 750. $^1$H NMR ($CDCl_3$), δ: 9.49 (s, 8 H, β-H in pyrrole); 5.77 (s, 8 H, Cp); 5.25 (s, 8 H, Cp); −1.37 (s, 2 H, NH). MS (FAB), *m/z*: 1119 $[MH]^+$, 1034 $[M-3CO]^+$, 727 $[M-12CO-Mn]^+$, 672 $[M-12CO-2Mn]^+$.

**Compound 2.** Found (%): C, 60.14; H, 3.30; N, 6.68. $C_{43}H_{23}N_4O_9Mn_3 \cdot 4/3C_6H_6 \cdot CH_3CN$*. Calculated (%): C, 60.64; H, 3.26; N, 6.67. UV ($CHCl_3$), $\lambda_{max}$/nm (log ε): 460 (5.04), 562 (3.97), 600 (4.30), 653 (4.18), 687 (4.18); ($CHCl_3$—$CF_3COOH$), $\lambda_{max}$/nm: 463, 480, 733. $^1$H NMR ($CDCl_3$), δ: 9.30 (br.s, 4 H); 9.12 (br.s, 2 H); 8.91 (br.s, 2 H, β-H in pyrrole); 6.01 (m, 4 H); 5.96 (m, 2 H); 5.31 (m, 6 H, Cp); −2.5 (br.s, 3 H, NH). MS (FAB), *m/z*: 905 $[MH]^+$, 820 $[M-3CO]^+$, 597 $[M-9CO-Mn]^+$, 541 $[M-9CO-2Mn-H]^+$.

This work was supported by the Russian Foundation for Basic Research (Project 93-03-5827) and the Russian State Scientific and Technical Program "Ecologically safe processes in chemistry and chemical technology" (Project 4.3.405).

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* The presence of solvating molecules of benzene, chloroform, acetonitrile, and hexane in the analytical samples of compounds **1** and **2** agrees with NMR spectroscopy data.

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*Received December 29, 1993;*
*in revised form February 15, 1994*