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Synthesis and unusual spectroscopic properties of diformyltetraarylporphyrins

Andrei F. Mironov,*[a] Michael A. Grin,[a] Tat'yana V. Moskal'chuk,[a] Alexander S. Shashkov[b] and Boris V. Lokshin[c]

[a] *M. V. Lomonosov Moscow State Academy of Fine Chemical Technology, 117571 Moscow, Russian Federation.*
Fax: +7 095 434 8711; e-mail: httos.mitht@g23.relcom.ru
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.*
Fax: +7 095 135 5328
[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation.*
Fax: +7 095 135 5085

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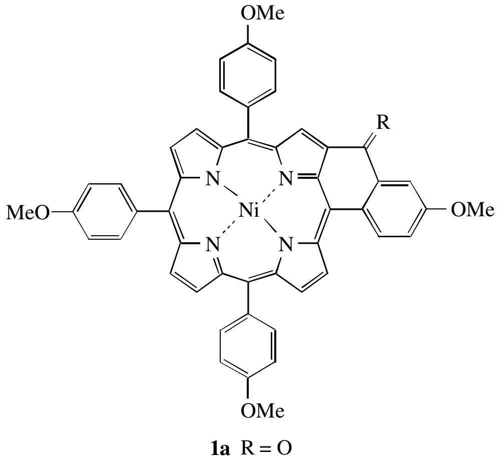
The mutual arrangement of two formyl groups in the nickel complex of tetra-*meso*-(*p*-methoxyphenyl)porphyrin has a strong effect on the spectroscopic characteristics of porphyrins.

Although formylation in the porphyrin series is a well-studied reaction,[1–3] the introduction of the second or more formyl groups into the macrocyclic ring of a porphyrin is not clearly understood. We faced this problem in the formylation of the nickel complex of 2-formyl-tetra-*meso*-(4-methoxyphenyl)-porphyrin **2**. We performed the Vilsmeier reaction and found that it resulted in compounds with colours that varied from red to green. It is well known that a green colour is characteristic of chlorin structures rather than porphyrins.[4] Because the reaction products exhibited these unusual colours, we examined this reaction in more detail. We took into account published data[4–6] on the condensation of a β-formyl group with the neighbouring *meso*-phenyl substituent in the presence of strong acids to form chlorin-like structures **1a**,**b**. In our case, these reactions can be catalysed by $POCl_3$ on the introduction of the second formyl group.

A common fraction of diformylsubstituted porphyrins **3** and **4** in 70% total yield was separated by chromatography after the Vilsmeier formylation of mono-formylsubstituted porphyrin **2**. The chromatographic separation of the resulting substances on high-performance TLC plates exhibited two closely spaced zones. The upper zone was green (α-band at 605 nm), and the lower zone was red (558 nm). The corresponding products will be referred to as Green- and Red-porphyrins.



1a R = O
1b R = 2H

Based on published data,[4] we suggested the intramolecular cyclization of the first formyl group with the formation of compounds like **1a** and **1b**, which were reported to be green and red, respectively. However, we experimentally found that cyclization was not observed in our case; consequently, the colour difference between the porphyrins is associated with other reasons.

Data obtained by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry suggest that, indeed, these are isomeric diformyl-substituted porphyrins.[†] The high-resolution mass spectra of Green- and Red-porphyrins exhibited the peaks of molecular ions with *m*/*z* 846.1984 and 846.1950, which correspond to the empirical formula $^{58}NiC_{50}H_{36}N_4O_6$ with *m*/*z* 846.1988.

The arrangement of formyl groups in Green- and Red-porphyrins was found using ^{1}H and ^{13}C NMR spectroscopy (Bruker DRX 500 instrument). Their structures were proposed based on two-dimensional ^{1}H and ^{13}C HSQC and HMBC NMR spectra with the use of the standard software from Bruker.

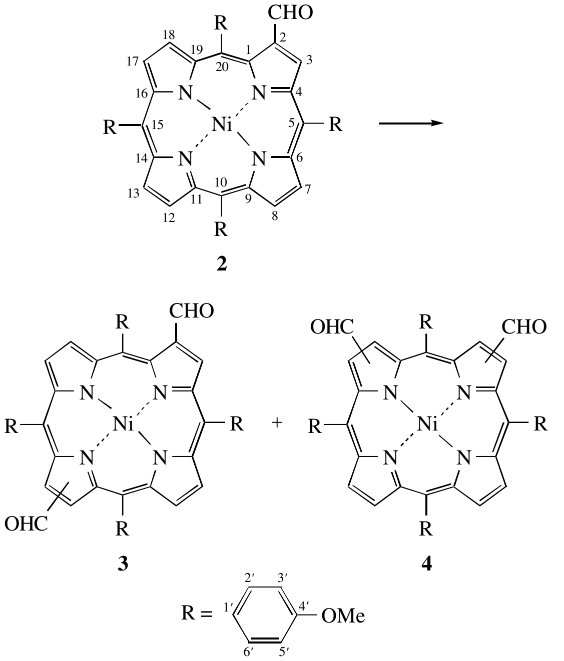
The formyl groups of Green-porphyrin exhibited one ^{13}C signal with a chemical shift of 187.84 ppm. Four closely spaced signals in the region 9.29–9.28 ppm correspond to the two protons of these groups and two neighbouring β-protons in the ^{1}H NMR spectra. The other four β-protons in unsubstituted pyrrole rings exhibited chemical shifts at 8.73–8.70 ppm. The ^{13}C NMR signals of β-carbon atoms in substituted pyrroles appeared at 136.36 and 136.12 ppm, whereas in unsubstituted pyrroles, at 133.46, 133.39 and 133.29 ppm. In the ^{1}H NMR spectrum, two singlets with equal intensities (six protons in each) at 4.06 and 4.04 ppm correspond to four methoxy groups, and carbon atoms manifested themselves as two signals at 55.57 and 55.54 ppm in the ^{13}C NMR spectrum.

The data suggest the high symmetry of Green-porphyrin. On

[†] The optical absorption spectra of the test compounds were recorded on a Jasco-7800 instrument. The ^{1}H NMR spectra were measured on a Bruker DRX-500 instrument in $CDCl_3$ solutions using TMS as an internal standard. The ^{13}C NMR spectra were interpreted using two-dimensional heteronuclear HSQC and HMBC spectra and Bruker software. The HMBC experiment was minimised for ^{1}H/^{13} KCCB 8 Hz. The IR spectra were recorded on a Nicolet Magna-750 spectrometer with a resolution of 2 cm^{-1} in KBr. The high-resolution mass spectra were measured on a Micromass Autospec Mass Spectrometer (70 eV EI, 200 °C).

Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$) δ: 4.04–4.06 (2s, 12H, OMe), 7.22–7.24 (m, 8H, *m*-phenyl H), 7.87–7.92 (m, 8H, *o*-phenyl H); 9.06–8.73 (m, 4H, β-H), 9.29 and 9.27 (2s, 2H, β-H nearby CHO), 9.3 and 9.28 (2s, 2H, CHO). ^{13}C NMR ($CDCl_3$) δ: 187.84 (CHO), 159.8 (4′-C), 145.4, 145.3, 144.3, 144.1 (1,4,11,14-C), 142.3, 142.1, 141.9, 140.7, 140.4 (6,9,16,19-C); 136.4, 136.1 (β-C in substituted pyrroles), 135.1, 135.0, 134.9 (2′,6′-C), 133.5, 133.4, 133.3 (β-C in unsubstituted pyrroles), 132.8 (1′-C nearby CHO), 131.8 (other 1′-C), 122.0, 121.6 (*meso*-C close to CHO), 118.6, 118.2 (other *meso*-C), 113.2 (3′,5′-C nearby CHO), 112.8 (other 3′,5′-C); 55.54 and 55.57 (OMe). UV [$CHCl_3$, λ_{max}/nm (rel. intensity)]: 443 (1), 520 (0.01), 559 (0.013), 605 (0.10). IR, ν/cm^{-1}: 1669, 1728 (CHO). EI HRMS, *m*/*z*: 846.1984 ($^{58}NiC_{50}H_{36}N_4O_6$ requires 846.1988).

For **4**: ^{1}H NMR ($CDCl_3$) δ: 4.04–4.06 (m, 12H, OMe), 7.21–7.24 (m, 8H, *m*-phenyl H), 7.86–7.96 (m, 8H, *o*-phenyl H), 8.66–8.75 (m, 4H, *m*,β-H), 9.32, 9.30, 9.26 and 9.25 (m, 2H, β-H nearby CHO), 9.29, 9.27 and 9.11 (3s, 2H, CHO). ^{13}C NMR ($CDCl_3$) δ: 187.6, 187.7, 187.9 (CHO), 161.1, 160.5, 160.3, 159.8, 159.6 (4′-C), 145.6, 145.4, 145.1, 144.2, 143.7, 142.8 (1,4,6.9-C), 142.3, 142.0, 141.2, 140.9, 140.6 (11,14,16,19-C), 136.5, 135.7 (β-C in substituted pyrroles), 135.9, 135.1, 135.07, 135.0, 134.9, 134.8 (2′,6′-C), 133.7, 133.5, 133.4, 133.3, 133.1, 133.0 (β-C in unsubstituted pyrroles), 132.8, 132.5 (1′-C nearby CHO), 132.1, 131.7 (other 1′-C), 121.7, 121.5, 120.9 (*meso*-C nearby CHO), 119.7, 119.4, 118.2 (other *meso*-C), 113.7, 113.2, 112.8, 112.7 (3′,5′-C), 55.56 (OMe). UV [$CHCl_3$, λ_{max}/nm (rel. intensity)]: 449 (1), 558 (0.1), 605 (sh, 0.02). IR, ν/cm^{-1}: 1667 (CHO). EI HRMS *m*/*z*: 846.1950 ($^{58}NiC_{50}H_{36}N_4O_6$ requires 846.1988).



this basis, we concluded that formyl groups are arranged at the opposite pyrrole rings. Consequently, Green-porphyrin exhibits the structure of **3**. In this case, two similar isomers can occur with the second formyl group at the 12- or 13-position. This was also supported by the presence of two doubled *meso*-^{13}C NMR signals at 122.02 and 121.62 ppm for *meso*-bridges adjacent to formyl groups and at 118.56 and 118.25 ppm for more distant *meso*-bridges. Isomers were formed in almost equal amounts, as follows from the intensities of the above signals.

Red-porphyrin exhibited spectra that are more complex. The formyl groups exhibited ^{13}C NMR signals at 187.88, 187.69 and 187.59 ppm and the corresponding proton signals at 9.29, 9.27 and 9.11 ppm. Two β-H neighbouring with formyl groups exhibited chemical shifts of 9.32, 9.30, 9.26 and 9.25 ppm in this region, whereas four protons in unsubstituted pyrrole rings exhibited a group of upfield signals at 8.75–8.66 ppm. The ^{13}C NMR signals of β-carbon atoms in pyrroles with formyl groups appeared at 136.45 and 135.72 ppm. The protons of methoxy groups exhibited five partially overlapping signals in the region 4.06–4.04 ppm with a total intensity of 12H, and carbon atoms exhibited a signal at 55.56 ppm. The arrangement of formyl groups in Red-porphyrin most strongly affected the chemical shifts of ^{13}C *meso*-bridges. The neighbouring atoms exhibited three signals at 121.68, 121.51 and 120.95 ppm, and atoms that are more distant also exhibited three upfield peaks at 119.69, 119.36 and 118.20 ppm.

Based on the above data, we concluded that formyl groups in Red-porphyrin are arranged at neighbouring pyrrole rings and hence it corresponds to the structure of **4**.

Formyl groups in neighbouring pyrrole rings have almost no effect on the general structure of the macrocyclic ring. This is evident from the optical absorption spectra of isomeric porphyrins **4** and the IR spectra, in which the $\nu_{C=O}$ stretching vibrations of formyl groups correspond to 1667 cm^{-1}, which is typical of formylporphyrins.[7]

It was mentioned above that, if formyl groups are arranged at the opposite pyrrole rings, the colour is green, and the optical absorption spectra of compound **3** exhibit a maximum at 605 nm, which is not typical of Ni porphyrins. However, the main difference is associated with the IR spectrum, which exhibits a less intense band at 1728 cm^{-1} along with an ordinary band at 1669 cm^{-1}. This is a very strong shift of $\nu_{C=O}$ for formylporphyrins,[3] which was not observed previously. The unusual spectral characteristics of porphyrin **3** can be explained by a distortion of the macrocyclic ring and its aromatic character and by the removal of a formyl group from conjugation with the macrocyclic ring. The former explains the green colour of the porphyrin, and the latter explains the shift of stretching vibrations of the formyl group to the region typical of aliphatic aldehydes.

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