Experimental Section

The synthesis of [6]-polyurethane is given as a typical example: A solution of 5-amino-1-pentanol (9.69 mmol, 1.00 g) in chloroform (2 mL) was injected by a syringe under the surface of a stirred solution of di-*tert*-butyltricarbonate (10.66 mmol, 2.80 g) in chloroform (30 mL). The solution was stirred for 10 min at room temperature under an argon atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 3.67$ (q, $^3J = 6.0$ Hz, 2H; CH_2OH), 3.32 (t, $^3J = 6.6$ Hz, 2H; CH_2NCO), 1.55 (br.m; 4H; $CH_2CH_2OH + CH_2CH_2NCO$), 1.40 (m, $^3J = 6.7$ Hz, 2H; CH_2 $CH_2CH_2CH_2$ CH_2); IR ($CHCl_3$): $\tilde{\nu} = 3396$ (br.s), 2971 (m), 2274 (s) cm^{-1}.

Zirconium(IV) acetylacetonate (0.1 mol%) was added, and the polymerization was carried out for 20 h with continuous stirring under argon at room temperature. The turbid reaction mixture was precipitated in diethyl ether (150 mL), and the polymeric product was collected by suction filtration in a yield of 0.81 g (63%). M.p. 127 °C; decomposition at 200 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 20 °C, TMS): $\delta = 7.04$ (br.t, 0.9H; N*H trans* conformer), 6.72 (br.m, 0.1H; N*H cis* conformer), 3.89 (t, $^3J = 6.2$ Hz, 2H; CH_2O), 2.95 (q, $^3J = 6.0$ Hz, 2H; CH_2N), 1.50 (m, $^3J = 7.2$ Hz, 2H; CH_2CH_2O), 1.40 (m, $^3J = 7.7$ Hz, 2H; CH_2CH_2N), 1.28 (m, $^3J = 6.6$ Hz, 2H; $CH_2CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 100 °C, TMS): $\delta = 156.4$ (*C*=O), 63.5 (CH_2O), 40.1 (CH_2N), 29.4 (CH_2CH_2O), 28.7 (CH_2CH_2N), 26.0 ($CH_2CH_2CH_2CH_2CH_2$); IR (KBr): $\tilde{\nu} = 3318$ (br.s), 2944 (m), 2870 (w), 1684 (s), 1535 (s), 1263 (s) cm^{-1}; elemental analysis (%) for $(C_6H_{11}NO_2)_n$ calcd: C 55.80, H 8.58, N 10.85; found: C 55.46, H 8.67, N 10.55.

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Isoporphycene: The Fourth Constitutional Isomer of Porphyrin with an N_4 Core—Occurrence of *E*/*Z* Isomerism**

Emanuel Vogel,* Peter Scholz, Ralf Demuth, Christoph Erben, Martin Bröring, Hans Schmickler, Johann Lex, Georg Hohlneicher,* Dominik Bremm, and Yun-Dong Wu*

Dedicated to Professor Satoru Masamune on the occasion of his 70th birthday

The synthesis of porphycene (**1**) in 1986[1] led to the realization that, in principle, no less than seven constitutional isomers of porphyrin with an N_4 core are possible.[2] Unlike porphyrin, its constitutional isomers contain one or two formal double bonds and may therefore give rise to *E*/*Z* isomerism. After **1** was shown to match porphyrin in many of its properties, it was clear that the isomers open a promising new chapter of porphyrin chemistry.[3] If a further incentive for the synthesis of the isomers was needed, this was provided by the inverted porphyrins discovered simultaneously by a Japanese and a Polish group.[4]

Porphycene (**1**), which is approximately 2 kcal mol^{-1} more stable than porphyrin according to ab initio calculations (BLYP/6-31G** method), has meanwhile been joined by hemiporphycene (**2**)[6] and corrphycene (**3**; each as octaalkyl derivatives).[7] Compounds **2** and **3** follow **1** on the stability scale of the constitutional isomers and are 5 and 12 kcal mol^{-1}, respectively, higher in energy than porphyrin.[5] Similar to porphyrin, **1**–**3** (see Scheme 1) are excellent complexing agents; this could not be predicted with certainty as the N_4 core of the three isomers covers a smaller area and deviates more or less strongly from the square shape. Thus, a multitude of comparative investigations of the metal complexes of the isomers and the corresponding metalloporphyrins suggested itself.

The isoporphycenes [porphyrins-(3.0.1.0)] **4** and **5** (Scheme 1), in fourth place on the stability scale of the isomers,[5] are not only interesting as complexing agents and for other porphyrin-relevant properties, but also demand attention under the aspect of stereoisomerism. Other than in the case of the constitutional isomers **1**–**3**, for which the *Z* isomer is strongly favored energetically over the *E* isomer, the two isoporphycene isomers only differ slightly (PM3) or

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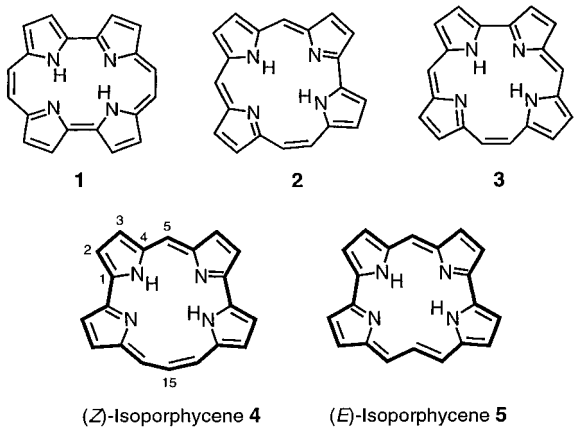
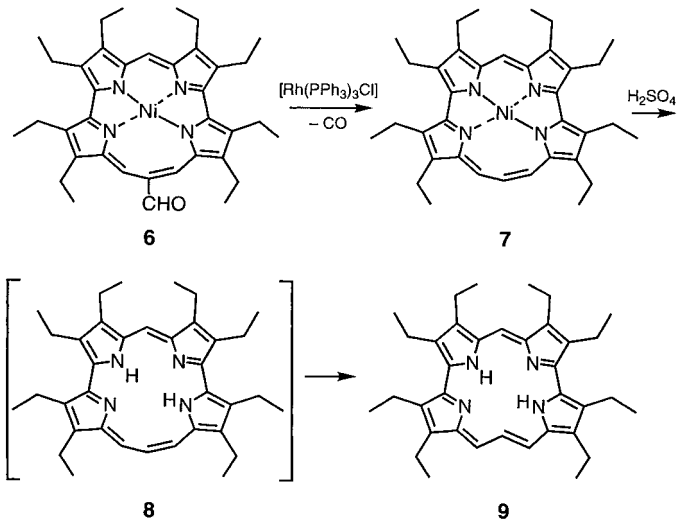


PM3	23.6	24.9
BLYP/6-31G**//3-21G	19.0	26.2

Scheme 1. The known constitutional isomers of porphyrin with an N_4 core (**1**–**3**) and the fourth isomer whose synthesis appears feasible, (*Z*)/(*E*)-isoporphycene (**4**/**5**). The relative energies [kcal mol^{-1}], with respect to porphyrin, according to the PM3 and the BLYP/6-31G**//3-21G methods[5] for the stereoisomers **4** and **5** are given.

moderately (BLYP/6-31G**) in their energy, so that their parallel existence seemed possible. However, it was uncertain whether **4** and **5** are sufficiently stable to be isolated in substance owing to their already considerable relative energy (with respect to porphyrin). Access to the stereoisomeric isoporphycenes—in the form of the octaethyl compounds **8** and **9** for reasons of solubility—was promised by the



demetalation of the metalloisoporphycenes recently obtained by template synthesis.[8] We can now report that the octaethyl isoporphycene ligand was liberated from the nickel complex **7**, isolated, and characterized.

A number of metal complexes of 15-formyl-(*Z*)-octaethylisoporphycene, especially the nickel complex **6**, are accessible from 1,17-diformyl-2,3,6,7,11,12,15,16-octaethyl-*a*,*c*-bisnor-*b*-bilene by a reaction cascade initiated by template formation with suitable metal ions.[8] When **6** was heated with tris(triphenylphosphane)rhodium(I) chloride (Wilkinson's catalyst) in benzonitrile under reflux (2 h), smooth decarbonylation took place to provide complex **7**, which was obtained as black needles with metallic sheen (m.p. 145–146 °C, yield 60 %) after chromatography on silica gel with dichloromethane/*n*-hexane (1/1) and crystallization from 2-propanol. It follows from the ^{1}H NMR spectrum that the isoporphycene ligand in **7** has the *Z* configuration, as the signals for H15 can be found similarly far downfield ($\delta = 9-10$) as those for the neighboring protons H14 and H16.

Complex **7** was characterized by X-ray crystallographic analysis. Two independent molecules are found in the elementary cell which have an approximately saddle-shaped (slightly differing) appearance due to a contraction of the ligand caused by the nickel ion. Further information on the structure of **7** will be given in a comparison with the molecular structures of the nickel complexes of octaethylporphyrin, octaethylporphycene, octaethylhemiporphycene, and octaethylcorrphycene.[9]

To liberate the ligand, **7** was treated with concentrated sulfuric acid at room temperature, the reaction mixture was poured on ice after 15 h, and sodium hydroxide (slightly less than the amount of sulfuric acid used) and then potassium carbonate were added at 0 °C (color change from green to red). After conventional workup, chromatography of the product on silica gel with dichloromethane/ethyl acetate (6/1) yielded two fractions, of which the first (brown) contained the starting material and the second (dark red) the free ligand. The ligand was obtained as rhombic, violet crystals (m.p. 129 °C, yield 23 %) from a small amount of *n*-hexane after storing of the solution at −20 °C and was identified as (*E*)-octaethylisoporphycene (**9**). As expected, **9**, which is stable in the crystalline state, is chemically much more reactive than its analogues **1**–**3**.

The surprising formation of **9**, combined with a change in configuration, on demetalation of the nickel complex **7** is verified by the ^{1}H NMR spectrum (Figure 1, Table 1), recorded at low temperature in order to freeze out dynamic

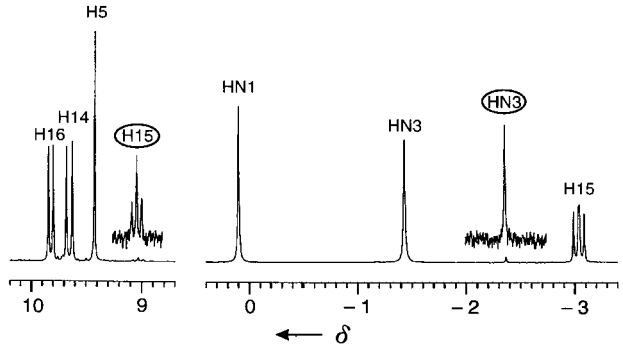


Figure 1. ^{1}H NMR spectrum of **9**/**8** (300 MHz, $CD_2Cl_2/CF_2Br_2/Al_2O_3$, 205 K). The encircled protons belong to (*Z*)-isoporphycene (**8**); further signals for **8** were assigned by two-dimensional experiments.

processes. The most striking feature of the spectrum is the upfield position of the H15 signals; proton H15 must therefore be located in the shielding area of the diamagnetic ring current assumed to be present in **9**. This unambiguously proves the *E* configuration of **9**. The porphyrinoid aromatic nature of the new constitutional isomer of porphyrin, which is already indicated by the chemical shift of H15, is supported by

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Table 1. Selected physical data for the compounds **7** and **9**–**13** (^{1}H NMR: 300 MHz; ^{13}C NMR: 75.5 MHz; IR: CsI; UV/Vis: CH_2Cl_2); correct elementary analyses for **7**, **9**, and **11**.

7: M.p. 145–146 °C (from 2-propanol); ^{1}H NMR ($CDCl_3$): $\delta = 9.67$ (d, 2H; H14,16), 9.42 (s, 1H; H5), 8.98 (t, 1H; H15), 4.03 (q, 4H; H11a,19a), 3.95 (q, 4H; H12a,18a), 3.90 (q, 4H; H2a,8a), 3.84 (q, 4H; H3a,7a), 1.79 (t, 6H; H3b,7b), 1.76 (t, 6H; H12b,18b), 1.69 (t, 6H; H11b,19b), 1.68 (t, 6H; H2b,8b); ^{13}C NMR ($CDCl_3$): $\delta = 146.03$, 145.81, 144.94, 142.54, 136.89, 135.24, 135.15, 112.01, 110.22, 101.07, 20.97, 20.68, 20.55, 19.68, 18.78, 18.59, 18.51, 18.38; IR: $\tilde{\nu} = 2964$, 2930, 2869, 1591, 1465, 1446, 1372, 1218, 1165, 1144, 1121, 1053, 1021, 956 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (17800), 340 (12600), 403 (106600), 489 (13600), 534 (8500), 616 (7000), 662 nm (3100); MS (FAB): *m*/*z* (%): 590 (100) [M^+]

9: M.p. 129 °C (from *n*-hexane at −20 °C); ^{1}H NMR ($CD_2Cl_2/CF_2Br_2/Al_2O_3$, 205 K): $\delta = 9.82$ (d, 1H; H16), 9.65 (d, 1H; H14), 9.42 (s, 1H; H5), 3.90 (q, 2H; H2a), 3.88 (q, 2H; H3a), 3.84 (q, 2H; H11a), 3.76 (q, 2H; H8a), 3.73 (q, 2H; H7a), 3.72 (q, 2H; H12a), 3.68 (q, 2H; H19a), 3.56 (q, 2H; H18a), 1.73 (t, 9H; H2b,3b,7b), 1.72 (t, 3H; H8b), 1.70 (t, 3H; H12b), 1.66 (t, 3H; H18b), 1.59 (t, 3H; H11b), 1.52 (t, 3H; H19b), 0.10 (br s, 1H; HN1), −1.43 (br s, 1H; HN3), −3.04 (dd; 1H; H15); ^{13}C NMR (CD_2Cl_2/CF_2Br_2, 205 K): $\delta = 154.05$, 149.17, 148.79, 146.68, 145.70, 144.81, 140.93, 140.01, 137.41, 135.57, 133.43, 133.28, 132.06, 131.68, 129.33, 127.77, 127.06, 124.22, 115.70, 104.71, 20.23, 20.11, 20.02, 19.92, 19.29, 19.12 (2×), 18.99, 18.99, 18.69 (3×), 18.37 (3×), 18.18; IR: $\tilde{\nu} = 3398$, 3357, 2964, 2930, 2868, 1579, 1551, 1488, 1463, 1315, 1284, 1173, 1144, 1123, 1061, 1054, 1014, 1000, 990, 950, 858, 851, 740 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 354 (21800), 434 (117200), 558 (5700), 615 (4700), 672 nm (6550); MS (FAB): *m*/*z* (%): 535 (100) [$(M+1)^+$], 534 (24) [$(M)^+$]

10 (= $(H_2$-**9**$)^{2+}$): ^{1}H NMR ($CDCl_3/CF_3COOH$): $\delta = 10.54$ (d, 2H; H14,16), 10.32 (s, 1H; H5), 4.04 (q, 4H; H2a,8a), 3.99 (q, 4H; H3a,7a), 3.91 (q, 4H; H11a,19a), 3.78 (q, 4H; H12a,18a), 1.76 (t, 6H; H12b,18b), 1.75 (t, 6H; H2b,8b), 1.73 (t, 6H; H3b,7b), 1.64 (t, 6H; H11b,19b), −0.87 (br s, 2H; HN3,4), −1.69 (br s, 2H; HN1,2), −5.80 (t, 1H; H15); ^{13}C NMR ($CDCl_3/CF_3COOH$): $\delta = 146.01$, 143.90, 142.03, 137.93, 137.75, 135.95, 135.77, 133.55, 131.56, 126.80, 106.86, 20.69 (2×), 20.19, 19.88, 17.58, 17.17, 16.82, 16.71; UV/Vis (CH_2Cl_2/CF_3COOH): λ_{max} (ε) = 311 (11800), 365 (17700), 408 sh (63100), 428 (228500), 506 (5300), 549 (9200), 597 (7800), 652 nm (14200)[a]

11 (= Cu-(**9** − 2H)): M.p. 164–165 °C (from CH_3OH/CH_2Cl_2); IR: $\tilde{\nu} = 2963$, 2929, 2868, 1578, 1522, 1477, 1457, 1449, 1406, 1372, 1314, 1265, 1214, 1168, 1143, 1121, 1053, 1021, 1005, 954 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 334 (17600), 374 (34800), 438 (57400), 456 (115400), 562 (8000), 584 nm (8600); MS (FAB): *m*/*z* (%): 595 (100) [M^+]

12/**13**: M.p. (*E*/*Z* mixture) 234–236 °C (from CH_3OH/CH_2Cl_2); *E* isomer: ^{1}H NMR ($CDCl_3$): $\delta = 9.53$ (d, 2H; H14,16), 9.41 (s, 1H; H5), 6.44 (m, 1H; *p*-H(pyridine)), 5.63 (m, 2H; *m*-H(pyridine)), 3.93 (q, 4H; H11a,19a), 3.89 (q, 4H; H2a,8a), 3.79 (q, 4H; H3a,7a), 3.67 (q, 4H; H12a,18a), 3.04 (br. m, 2H; *o*-H(pyridine)), 1.74 (t, 6H; H3b,7b), 1.71 (t, 6H; H11b,19b), 1.69 (t, 6H; H2b,8b), 1.67 (t, 6H; H12b,18b), −2.47 (t, 1H; H15); ^{13}C NMR ($CDCl_3$): $\delta = 146.77$, 144.90, 144.58, 144.20, 142.68, 141.80, 140.93, 138.02, 135.81, 133.39, 128.72, 124.60, 122.34, 106.60, 20.76, 20.26, 19.70, 19.34, 19.34, 19.13, 18.76, 18.63; *Z* isomer: ^{1}H NMR ($CDCl_3$): $\delta = 9.67$ (d, 2H; H14,16), 9.66 (s, 1H; H5), 8.92 (t, 1H; H15), 6.44 (m, 1H; *p*-H(pyridine)), 5.63 (m, 2H; *m*-H(pyridine)), 4.06 (q, 4H; H11a,19a), 3.94 (q, 4H; H12a,18a), 3.92 (q, 4H; H2a,8a), 3.86 (q, 4H; H3a,7a), 3.04 (br. m, 2H; *o*-H(pyridine)), 1.77 (t, 6H; H3b,7b), 1.74 (t, 6H; H11b,19b), 1.71 (t, 6H; H12b,18b), 1.62 (t, 6H; H2b,8b); ^{13}C NMR ($CDCl_3$): $\delta = 148.06$, 145.33, 144.52, 144.34, 144.20, 141.90, 139.62, 135.81, 135.59, 133.87, 122.34, 114.64, 107.79, 106.21, 20.76, 20.62, 19.90, 19.77, 18.87, 18.87, 18.71, 18.63; IR: $\tilde{\nu} = 2964$, 2929, 2868, 1602, 1564, 1446, 1485, 1464, 1400, 1373, 1311, 1216, 1154, 1140, 1122, 1061, 1039, 1017, 953, 861, 695, 632 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 449 (142800), 460 sh (82000), 557 (10000), 597 (9900), 667 nm (5800); MS (FAB): *m*/*z* (%): 596 (40) [$(M-py)^+$], 536 (100) [(octaethylisoporphycene)$^+$]; high-resolution MS (EI) calcd for $C_{41}H_{49}N_5Zn$: 596.284, found: 596.282

[a] The molar extinction coefficients given are valid under the assumption that **9** is protonated quantitatively. Attempts to obtain salts of **9** in substance through the use of various acids always led to decomposition products.

the observation that the signals of the remaining vinylic protons (H14, H16, and H5) appear relatively far downfield, whereas those of the N-bound protons are relatively far upfield. It follows from the determination of remote couplings that **9**, as is shown in the formula drawing, is present in the tautomeric form with the protons localized at N1 and N3. This is the most stable of the four possible NH tautomers according to calculations.[5] Because of the relatively strong N1−H···N2 hydrogen bond, the downfield NH signal is assigned to the proton at N1.

When the measuring temperature is raised above 298 K, a spectrum develops which corresponds to an (*E*)-octaethylisoporphycene with effective C_{2v}, C_s, or C_2 molecular symmetry (formal identity of the two halves of the molecule), depending on whether the ring skeleton of **9** is planar, concave, or twisted. According to this finding, **9** undergoes rapid (on the NMR time scale), isodynamic NH tautomerism at room temperature. From the coalescence temperature for the doublets of H14 and H16 (253 K), a Gibbs activation energy $\Delta G^{\neq}$ of 13.5 kcal mol^{-1} was determined for the NH tautomerism. This value is approximately 5 kcal mol^{-1} higher than that of octaethylcorrphycene (likewise with a trapezoidal N_4 core),[7a] which should be due to a larger N3···N4 distance and a certain steric hindrance caused by H15 of the, probably rate-determining, proton transfer between N3 and N4.

Additionally occurring signals of very low intensity at $\delta =$ 9.03 (H15) and −2.36 (HN3) in the ^{1}H NMR spectrum (300 MHz, 205 K) were a first indication that **9** is accompanied by approximately 2% of the *Z* isomer **8** (Figure 1). The presence of **8** became certain when 2D ROESY experiments allowed also the signals for H5, H14, and H16 of this isomer to be detected. As all attempts to separate **9** and **8** by recrystallization or with chromatographic methods (two-dimensional TLC and HPLC; also carried out under absence of light) remained unsuccessful, it is probable that the two compounds are in an extremely rapidly established acid-catalyzed equilibrium. An argument for the equilibrium hypothesis is not least the smooth reformation of **7** upon complexation of **9** with nickel ions.

In the presence of such an equilibrium, the observed quantity ratio of **9** and **8** (98:2) means that the difference in Gibbs energies ΔG^0 of the two isomers amounts to 2.5 kcal mol^{-1}, the *E* isomer being energetically favored. This result was the reason for the inclusion of the octaethyl derivatives **8** and **9** into the quantum chemical calculations, in order to take into account the steric interactions of the ethyl groups. Geometrical optimizations for the ethyl groups according to the PM3 method and for the isoporphycene skeleton according to the BLYP/3-21G** method led to the surprising result that the *E* isomer **9**—in reversal of the stability relations of **4** and **5**—is approximately 3.4 kcal mol^{-1} more stable than the *Z* isomer **8**. This is qualitatively in accordance with the experimental findings. A geometry optimization including all eight ethyl groups on the B3LYP/6-31G** level yielded a difference in energy of 1.1 kcal mol^{-1} in favor of **9**.[10]

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The UV/Vis spectrum of the *E* isomer **9** (bold-faced solid line in Figure 2; the influence of 2% of isomer **8** on the spectrum is negligible; see fluorescence excitational spectrum, Figure 3) contains a pronounced Soret band at 434 nm that

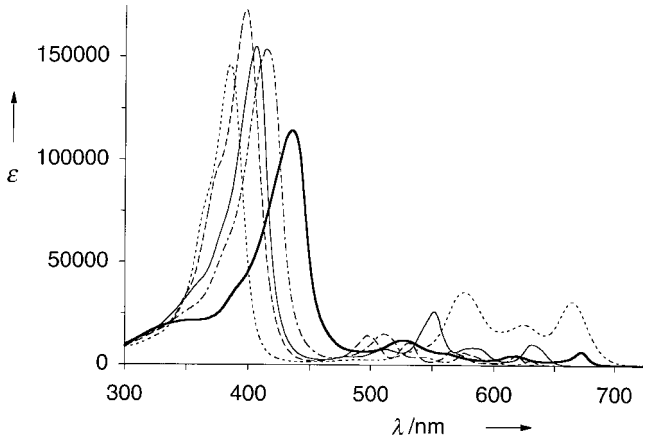

Figure 2. UV/Vis spectra (in CH_2Cl_2) of isoporphycene (**9**, ——) as well as porphyrin (– – –), porphycene (**1**, - - - -), hemiporphycene (**2**, ——), and corrphycene (**3**, – – – –), each as octaethyl-substituted compounds.

shows a bathochromic shift with respect to the corresponding bands of the octaethyl derivatives of porphyrin and **1** – **3** (also shown in Figure 2) and is distinctly less intensive. Q bands are found in the region of 558, 625, and 672 nm.

The UV/Vis spectroscopic characterization also of the *Z* isomer **8**, and thus its independent identification, was achieved with the help of low-temperature fluorescence spectroscopy (Figure 3).[11] The fluorescence of **8** becomes visible as a well-separated band at 646 nm besides the intensive emission at 673 nm, which can be assigned unambiguously to the *E* isomer **9** upon comparison with the absorption spectrum. The intensity ratio of the two bands, which depends on the chosen excitation wavelength, is of the order expected for the 2% share of **8** determined by NMR

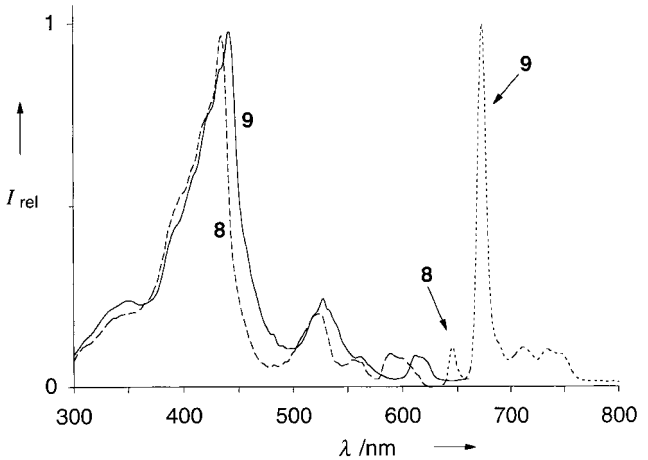

Figure 3. Fluorescence emission spectrum of **9** (containing 2% of **8**) (- - - -) as well as fluorescence excitation spectra of **9** (——) and **8** (– – –). Solvent 3-methylpentane, temperature 105 K, excitation wavelength 523 nm, emission wavelengths 673 nm (**9**) and 646 nm (**8**); ordinate: relative intensity (normalized to one). In the excitation spectra the first Q band is missing as it could not be observed owing to light scattering by the sample.

spectroscopy. The excitation spectra of the isomers **8** and **9** can be obtained by detection on one of the fluorescence signals. According to Figure 3, these spectra are very similar, with the bands of the *Z* isomer being shifted by 5 – 12 nm to shorter wavelengths.

According to a crystal structure analysis,[12] the ring skeleton of **9** is virtually planar (Figure 4). Only C15 protrudes slightly out of the ideal plane formed by the remaining skeleton C atoms and the N atoms (0.192 Å); this should be

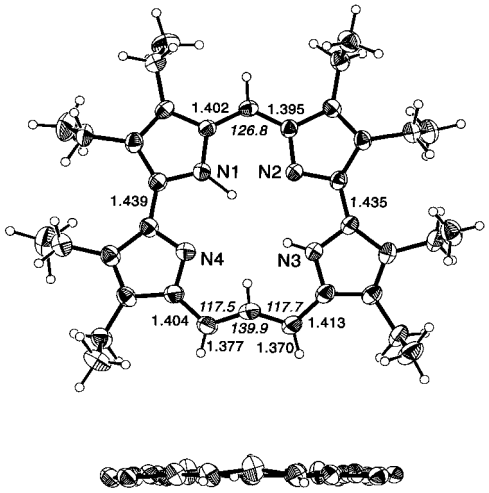

Figure 4. Structure of (*E*)-octaethylisoporphycene (**9**) in the crystal. Top: plan view; bottom: side view, without ethyl substituents. The ellipsoids correspond to the 40% probability level. Selected bond lengths [Å] and angles [°] are shown (standard deviations approximately 0.006 Å and 0.4°); further distances: N1–N2 2.826, N1–N4 2.541, N2–N3 2.541, N3–N4 3.909 Å.

due to the tendency of H15 to decrease the steric interaction with the hydrogen atom at N3. Nevertheless, the distance between H15 and HN3 remains very short (1.837 Å). The N-bound hydrogen atoms, which can be definitely localized, are in accordance with the conditions in solution at N1 and N3. The fact that **9** is a porphyrinoid aromatic compound is mirrored in the C–C bond lengths, especially those in the C13 to C17 unit (1.37 – 1.41 Å). An indication of the steric strain in **9** apparent from the calculations is the expansion of the C14-C15-C16 angle to 140°.

The octaethylisoporphycene **9** is N-protonated smoothly by trifluoroacetic acid—under retention of configuration—to the corresponding dication **10** (Table 1), which is stable in solution but decomposes when its isolation is attempted. The diprotonation is detectable by the fact that the signals for H5, H14, and H16 are shifted downfield by approximately 1 ppm (in analogy to porphyrin and the other isomers) and that for H15 is shifted upfield in a complementary way by no less than 2.8 ppm (to $\delta = -5.8$!). Protonated **9** must therefore sustain a sizeable diamagnetic ring current, although the presence of five hydrogen atoms on the inside of the molecule should lead to considerable deformation of the ring skeleton.

The availability of the free *E* isoporphycene ligand **9** led to the expectation that the range of metalloisoporphycenes accessible by means of template synthesis—apart from the nickel complex **7**, complexes of palladium,[8] vanadium

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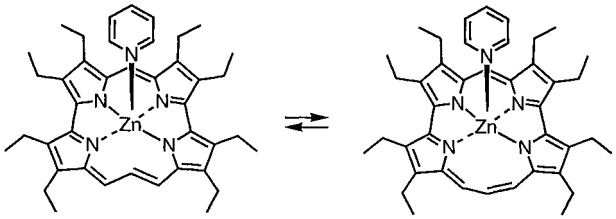
(VO),[13] platinum,[8] and copper[14] (**11**, Table 1; the two latter complexes are formed in only very low yields)—can be extended to complexes of other important metals. In view of the chemical sensitivity of **9**, however, successful metalation could only be expected if **9** was able to incorporate the metal ions in question rapidly. Surprisingly, **9** yielded the (pyridine)zinc complex **12**/**13** and the known copper complex **11** spontaneously and at room temperature, thus surpassing octaethylporphyrin in its complexation tendency towards zinc and copper ions despite the pronounced trapezoidal shape of its N_4 core.[15]



12 **13**

The zinc complex with an axial pyridine ligand obtained from **9** in dichloromethane/pyridine with methanolic zinc acetate solution turned out, in analogy to the palladium complex, to be a mixture of *E* and *Z* isomers (**12** and **13**, respectively), whose composition (60:40) was determined by means of the H15 NMR signals (triplet at $\delta = -2.5$ and 8.9, respectively).[16] It could not yet be established beyond doubt whether the paramagnetic copper complex **11** is the *E* and/or the *Z* isomer. Experiments towards the systematic investigation of the formation of metal complexes with **9** and **8** are under way.

With the synthesis of isoporphycene as the *E* isomer, a molecule distinctly more reactive than **1**–**3**, all of the constitutional isomers of porphyrin with an N_4 core that can be made according to thermodynamic considerations should now be in our hands. The remaining three isomers (each with *Z* configuration) are assumed to be only of fleeting existence as their relative energy increases by a further 9.9, 19.7, and 51.6 kcal mol^{-1}, respectively, based on **4**.[5] However, it cannot be ruled out completely that metal complexes of the first two of the three isomers are still stable compounds.

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