Expanded Porphyrins

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Double Ring Expansion from an Aromatic [18]Porphyrin(1.1.1.1) to an Antiaromatic [20]Porphyrin(2.1.2.1)

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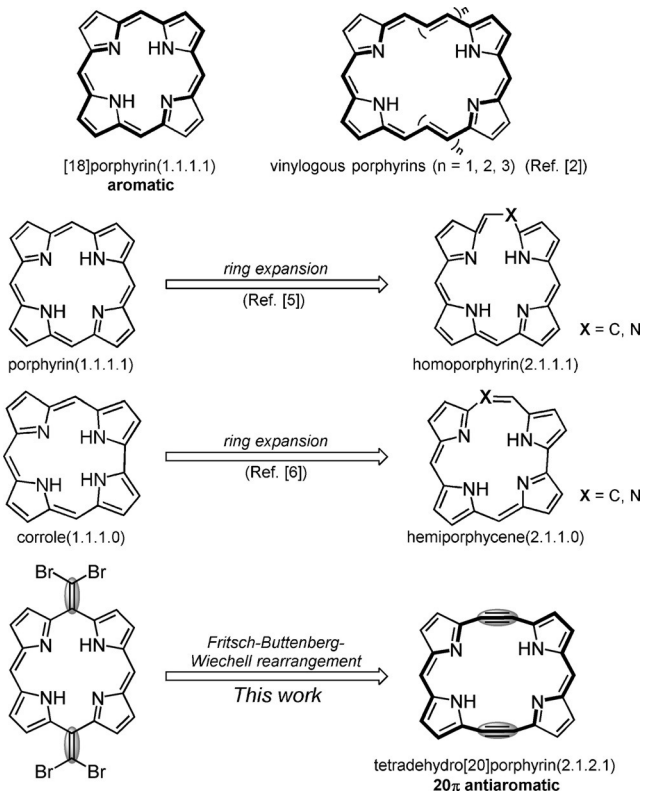
Abstract: *Double ring expansion from a 5,15-diarylporphyrin to a 5,16-diaryl-10,11,21,22-tetradehydro[20]porphyrin-(2.1.2.1) occurred through a reaction sequence consisting of oxidation with PbO_2 to 5,15-dioxoporphodimethene, a Corey–Fuchs reaction with tetrabromomethane in the presence of triphenylphosphine, and Fritsch–Buttenberg–Wiechell rearrangement triggered by tert-butyllithium. The obtained tetradehydro[20]porphyrin(2.1.2.1) and its mono- and dihydrogenated congeners exhibited 20π antiaromatic character, whereas overhydrogenated congeners bearing a saturated bridge were nonaromatic owing to disrupted π conjugation.*

Expanded porphyrins consisting of more than five pyrrole rings have been widely studied in light of their large and flexible structures, versatile electronic states, and rich coordination chemistry.[1] As another class of expanded porphyrins, so-called vinylogous porphyrins, which consist of four pyrrole rings and vinylene bridges, have been systematically studied by Franck and co-workers (Scheme 1).[2] Vinylogous porphyrins, such as [22]porphyrin(3.1.3.1) ($n=1$), [26]porphyrin(5.1.5.1) ($n=2$), and [30]porphyrin(7.1.7.1) ($n=3$), were synthesized by McDonald-type condensation reactions and shown to display remarkably intensified and redshifted Soret-like bands in accordance with their aromatic characteristics. Despite these studies, one of the most important vinylogous porphyrinoids, [20]porphyrin(2.1.2.1), has remained unexplored so far.[3] Importantly, [20]porphyrin-(2.1.2.1) should be antiaromatic when it takes on a planar conformation. Antiaromatic porphyrinoids are certainly often stable in the case of large expanded porphyrins[4] but become rather unstable on a small porphyrin platform, as confirmed by the syntheses of [16]- and [20]porphyrins.[5] These antiaromatic porphyrins displayed rather distorted structures to avoid serious instability owing to antiaromaticity.

Skeletal ring expansion would be quite useful for the synthesis of expanded porphyrins with unique structures and electronic properties but has rarely been reported so far.[6] As



Scheme 1. Vinylogous porphyrins ($n=1$, 2, and 3) and ring-expansion reactions.

interesting examples, Callot and co-workers reported ring-expansion reactions of porphyrins to give homoporphyrins[7a] and monoazahomoporphyrins,[7b] and Paolesse and co-workers reported the ring expansion of corroles to hemiporphycenes, porphyrins, and a monoazahemiporphycene.[8] Guilard and co-workers also discovered an interesting transformation of a corrole into a porphyrin.[9] Herein, we report an effective reaction sequence that enabled the ring expansion of a porphyrin to a tetradehydro[20]porphyrin(2.1.2.1). Our reaction sequence consists of oxidation, a Corey–Fuchs reaction, and Fritsch–Buttenberg–Wiechell rearrangement to give the tetradehydro[20]porphyrin(2.1.2.1) as a stable antiaromatic compound.[10,11]

We used a previously reported method[12] to prepare dioxoporphodimethene **2** in good yield by the oxidation of dimesitylporphyrin **1** with PbO_2 (Scheme 2). A Corey–Fuchs reaction of **2** with tetrabromomethane in the presence of triphenylphosphine gave tetrabromoporphoquinodimethane **3** as a key intermediate. The Fritsch–Buttenberg–Wiechell

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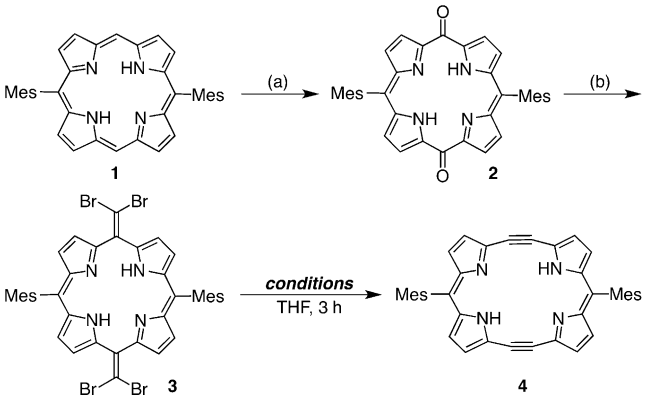


Scheme 2. Synthesis of **4**. Reagents and conditions: a) PbO_2, $CHCl_3$, AcOH, room temperature, 5 h, 76%; b) CBr_4, PPh_3, toluene, 80°C, 12 h, 84%.

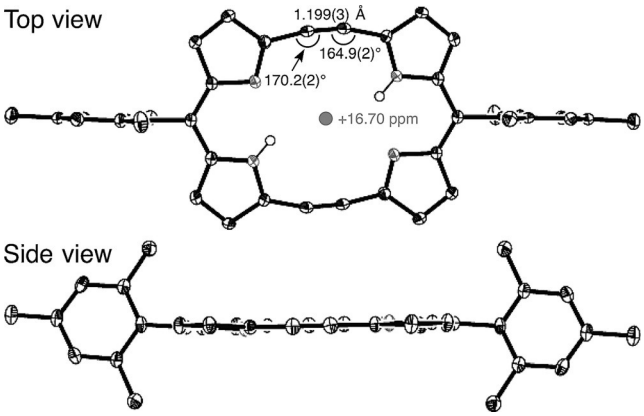


Figure 1. X-ray crystal structure and the NICS(0) value at the central point (gray dot) of **4**. Solvent molecules and hydrogen atoms, except for NH groups, are omitted for clarity. The thermal ellipsoids are scaled to 50% probability.

rearrangement of **3** was then attempted. Thus, **3** was treated with *n*-butyllithium (4.1 equiv) at −78°C in THF, and the reaction mixture was stirred at −40°C for 3 h. After the usual aqueous workup and column chromatography over silica gel, the desired tetradehydro[20]porphyrin(2.1.2.1) **4** was obtained in 3.5% yield (Table 1, entry 1). The use of *tert*-butyllithium (6.1 equiv) increased the yield of **4** (entry 2), and lowering of the reaction temperature to −98°C led to further improvement of the yield of **4** (entries 3 and 4). Finally, the treatment of **3** with *t*-butyllithium (6.1 equiv) at −98°C for 3 h gave **4** in 44% yield (Table 1, entry 5).

Table 1: Optimization of the reaction conditions.

Entry	Li reagent	*T*	Yield [%]
1	*n*BuLi (4.1 equiv)	−78→−40°C	3.5
2	*t*BuLi (6.1 equiv)	−78→−40°C	11
3	*n*BuLi (4.1 equiv)	−98→−40°C	12
4	*t*BuLi (6.1 equiv)	−98→−40°C	36
5	*t*BuLi (6.1 equiv)	−98°C	44

The structure of [20]porphyrin(2.1.2.1) **4** was revealed by X-ray diffraction analysis.[13] Importantly, [20]porphyrin-(2.1.2.1) **4** takes on a fairly planar conformation with a small mean-plane deviation (MPD)[14] of 0.028 Å, and the ethynyl moieties in the long sides deviate substantially from the line connecting the α positions of the pyrrole rings with bond angles of 170.2(2) and 164.9(2)° (Figure 1). The bond length of the C≡C triple bond is 1.199(3) Å, which is within the range of typical triple bonds.

Whereas the ^{1}H NMR spectrum of **1** features a typical spectral pattern of aromatic porphyrins, that of **4** shows two doublets at 4.81 and 4.69 ppm due to the β hydrogen atoms and a singlet at 24.24 ppm due to the NH hydrogen atoms, thus indicating its distinct paratropic ring current (Figure 2). In line with these data, the nucleus-independent chemical shift (NICS) value at the center of **4** was calculated to be +16.70 ppm.[15] Anisotropy of induced current density (AICD) calculations also support the antiaromaticity (see Figures S8 and S9 in the Supporting Information). Despite this distinct antiaromatic character, **4** is certainly stable and

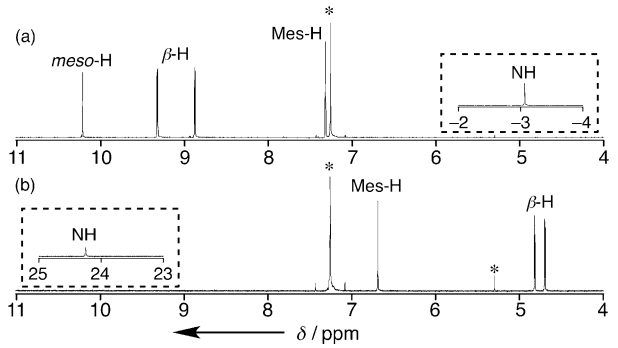


Figure 2. ^{1}H NMR spectra of a) **1** and b) **4** in $CDCl_3$ at room temperature. * indicates residual solvent peaks.

can be handled in the same way as usual organic molecules. Porphyrin **1** exhibits a sharp Soret band at 405 nm and a weak Q band at 500 nm in its UV/Vis/NIR absorption spectrum in CH_2Cl_2. On the other hand, tetradehydro[20]porphyrin-(2.1.2.1) **4** displays two broad absorption bands at 312 and 454 nm with a very weak absorption tail reaching around 1200 nm (Figure 3a). This weak absorption tail can be ascribed to the presence of low-energy dark states, which are a characteristic feature of antiaromatic porphyrinoids.[16] Transient absorption (TA) spectra of **1** exhibited a long decay component (10.3 ns). In sharp contrast, TA spectra of **4** showed very rapid double-exponential decay of two time constants of 0.3 and 7.0 ps (see Figure S9). The ultrafast decay dynamics of **4** can be explained in terms of the optically dark state of antiaromatic porphyrinoids.[16]

Hydrogenation of **4** with the Lindlar catalyst led to the production of a complex mixture containing over-reduced products. Milder hydrogenation of **4** with a Lindlar catalyst poisoned with quinoline[17] gave the dihydrogenated product **5** (36%) and tetrahydrogenated product **6** (3%) along with over-reduced products **7** (7%) and **8** (15%; Scheme 3).[18,19] Compound **6** is a genuine [20]porphyrin(2.1.2.1) according to the definition put forward by Gosmann and Franck.[2a] All the structures of these reduced products were revealed by X-ray

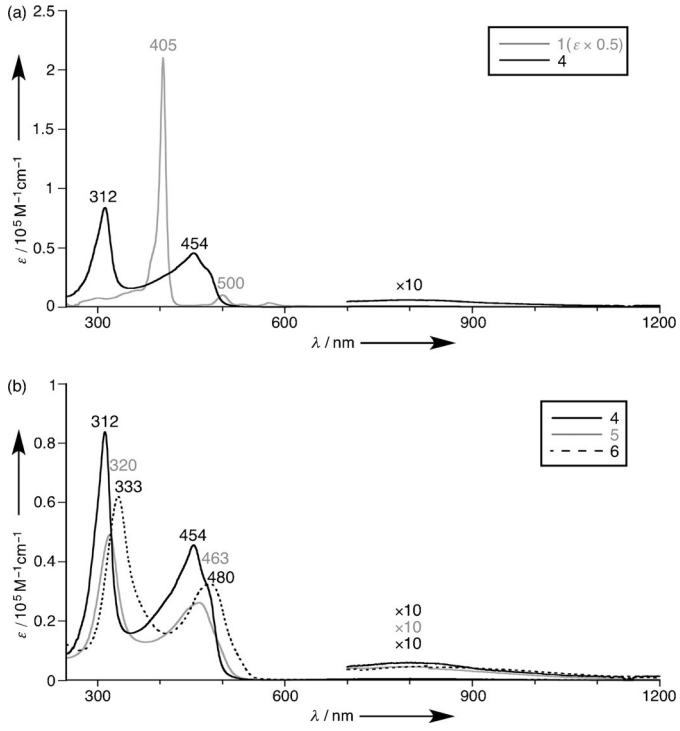
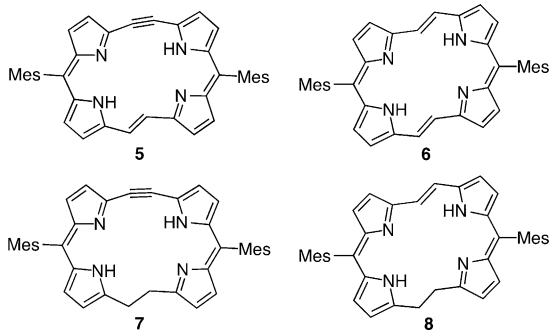


Figure 3. UV/Vis/NIR absorption spectra of a) **1** and **4** in CH_2Cl_2 and b) **4**, **5**, and **6** in CH_2Cl_2.



Scheme 3. Hydrogenated products **5**, **6**, **7**, and **8**.

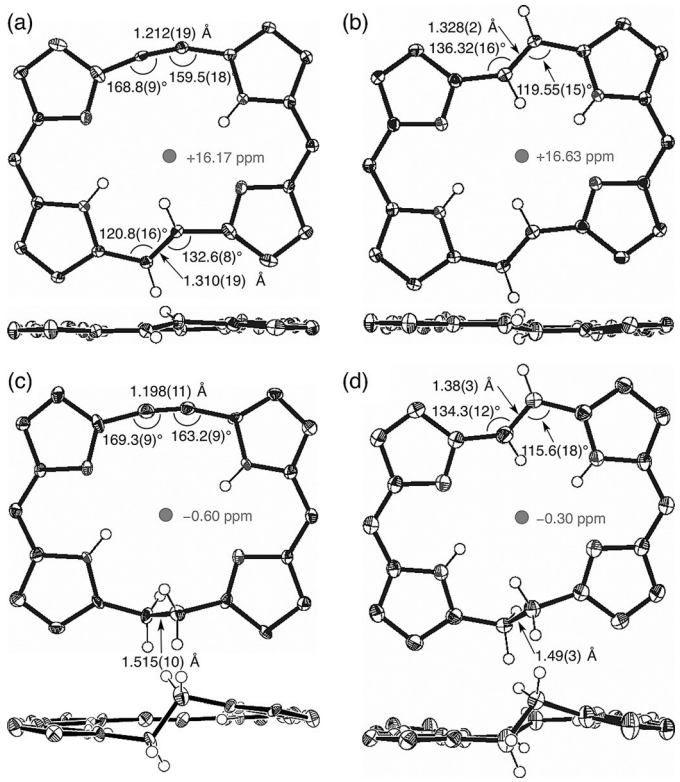


Figure 4. X-ray crystal structures and the NICS(0) values at the central point of a) **5**, b) **6**, c) **7**, and d) **8**. Top: top view; bottom: side view. Solvent molecules, mesityl groups, and pyrrolic hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 50% probability.

diffraction analysis (Figure 4).[13] Interestingly, both **5** and **6** possess *trans*-ethenyl sides, although hydrogenation with the Lindlar catalyst usually affords the *cis* olefin. The corresponding *cis* isomers were not observed in this reaction. DFT calculations estimated the total energy of *cis* isomers **5′** and **6′** to be 14.25 and 6.40 kcal mol^{-1} higher than those of **5** and **6**, respectively, thus indicating that the *trans* isomers **5** and **6** are much more stable (see the Supporting Information). The bond lengths of the ethynyl and *trans*-ethenyl sides of **5** are 1.212(19) and 1.310(19) Å, respectively, whereas the bond lengths of the *trans*-ethenyl linkers of **6** and **8** are slightly longer (1.328(2) Å for **6** and 1.38(3) Å for **8**). The ethynyl moiety of **5** is deformed to a large extent, with bond angles of 168.8(9) and 159.5(18)°. This deformation probably facilitates the further hydrogenation of **5**. The bond angles of the *trans*-ethenyl linkers in **6** are 136.32(16) and 119.55(15)°, thus indicating less structural distortion. The bond lengths of the saturated ethane linkers of **7** and **8** are 1.515(10) and 1.49(3) Å, respectively. The partially reduced products **5** and **6** display nearly planar conformations with MPD values of 0.049 and 0.052 Å, respectively, whereas the macrocycles in **7** and **8** deviate from planarity (0.147 Å for **7** and 0.155 Å for **8**).[14]

The ^{1}H NMR spectra of **5** and **6** also indicated paratropic ring currents: Doublet peaks due to the β hydrogen atoms were observed at high field in the range of 5.60–4.63 ppm and low-field singlet peaks due to the inner NH hydrogen atoms occurred at 24.68 and 27.14 ppm, respectively. The signal of the *trans*-ethenyl group of **6** was broad at room temperature but became a singlet observed at 11.24 ppm at 140 °C in [D_2]tetrachloroethane, thus indicating restricted rotation at room temperature and free rotation at 140 °C. At −94 °C in CD_2Cl_2, the signal became two doublets at 19.45 and 3.72 ppm for the inner and outer alkene hydrogen atoms, respectively, with $J = 17.0$ Hz, thus indicating frozen rotation of the *trans*-ethenyl group. The ^{1}H NMR spectra of **7** and **8** showed doublet peaks in the range of 6.98–6.40 ppm due to the β hydrogen atoms and singlet peaks at 12.71 and 13.99 ppm due to the inner NH hydrogen atoms, thus indicating their nonaromatic character. The NICS(0) values also support these assignments: Large positive values were found for **5** (+16.17 ppm) and **6** (+16.63 ppm), and negligible magnetic shielding for **7** (−0.60 ppm) and **8** (−0.30 ppm).[15] The hydrogenated products **5** and **6** displayed two broad absorption bands at 320 and 463 nm and at 333 and 480 nm,

respectively, along with weak and broad absorption tails (Figure 3b), similar to the absorption feature of **4**, whereas **7** and **8** did not display such weak absorption tails.

Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) experiments were conducted in CH_2Cl_2 against the ferrocene/ferrocenium ion couple (see the Supporting Information). Compound **4** exhibited two reduction potentials at −1.19 and −1.64 V and two oxidation potentials at 0.43 and 0.88 V. The electrochemical HOMO–LUMO gap (ΔE_{HL}) was determined to be 1.62 eV. This small HOMO–LUMO gap as compared to that of **1** is consistent with the antiaromatic character of **4**. Reduction products **5** and **6** also exhibited two reversible reduction waves at −1.24 and −1.69 V and at −1.29 and −1.77 V, and two reversible oxidation waves at 0.33 and 0.72 V and at 0.20 and 0.58 V, respectively. Both the first reduction potential and the first oxidation potential of **5** and **6** are higher than those of **4**. The electrochemical HOMO–LUMO gap of these three compounds decreases in the order **4** > **5** > **6**.

In summary, we developed a reaction sequence that enabled the double ring expansion of [18]porphyrin(1.1.1.1) to tetradehydro[20]porphyrin(2.1.2.1) **4**. The reaction sequence involves oxidation with PbO_2, a Corey–Fuchs reaction, and Fritsch–Buttenberg–Wiechell rearrangement. The hydrogenation of **4** with a Lindlar catalyst poisoned with quinoline afforded the partially hydrogenated products **5**, **6**, **7**, and **8**. Compounds **4**, **5**, and **6** are unprecedented genuine [20]porphyrin(2.1.2.1) analogues, which were shown to be fairly planar and thus antiaromatic but considerably stable under ambient conditions. The application of this synthetic strategy to other porphyrinoids is being actively pursued in our laboratory.

Acknowledgments

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Keywords: antiaromaticity · expanded porphyrins · porphyrins · rearrangement · vinylogous porphyrins

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[13] Crystallographic data for **4**: $C_{40}H_{32}N_4$, $2(CHCl_3)$; $M_w = 807.43$; monoclinic; $P2_1/n$ (No.14); $a = 13.170(5)$, $b = 9.418(3)$, $c = 15.367(5)$ Å; $\beta = 90.015(15)°$; $V = 1906.0(11)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.407$ g cm^{-3}; $R1 = 0.0428$ [$I > 2\sigma(I)$]; $wR2 = 0.1196$ (all data); GOF = 1.044; crystallographic data for **5**: $C_{40}H_{34}N_4$, $2(CHCl_3)$; $M_w = 809.44$; monoclinic; $P2_1/n$ (No.14); $a = 13.297(3)$, $b = 9.4395(18)$, $c = 15.301(3)$ Å; $\beta = 90.658(7)°$; $V = 1920.4(7)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.400$ g cm^{-3}; $R_1 = 0.0346$ [$I > 2\sigma(I)$]; $wR_2 = 0.0831$ (all data); GOF = 1.039; crystallographic data for **6**: $C_{40}H_{36}N_4$, $2(CHCl_3)$; $M_w = 811.46$; monoclinic; $P2_1/n$ (No.14); $a = 13.424(3)$, $b = 9.447(9)$, $c = 15.356(4)$ Å; $\beta = 92.076(9)°$; $V = 1946.1(9)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.385$ g cm^{-3}; $R_1 = 0.0339$ [$I > 2\sigma(I)$]; $wR_2 = 0.0904$ (all data); GOF = 1.067; crystallographic data for **7**: $C_{40}H_{36}N_4$, $2(CHCl_3)$; $M_w = 811.46$; monoclinic; $P2_1/n$ (No.14);

$a = 13.209(3)$, $b = 9.508(3)$, $c = 15.515(4)$ Å; $\beta = 91.891(7)°$; $V = 1947.5(9)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.384\ g\,cm^{-3}$; $R_1 = 0.0509$ [$I > 2\sigma(I)$]; $wR_2 = 0.1382$ (all data); GOF = 1.094; crystallographic data for **8**: $2(C_{40}H_{38}N_4)$; $M_w = 1149.48$; triclinic; $P\bar{1}$ (No.2); $a = 11.679(4)$, $b = 11.685(3)$, $c = 13.048(5)$ Å; $\alpha = 93.232(4)$, $\beta = 114.221(14)$, $\gamma = 93.519(8)°$; $V = 1614.3(9)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.182\ g\,cm^{-3}$; $R_1 = 0.0401$ [$I > 2\sigma(I)$]; $wR_2 = 0.1079$ (all data); GOF = 1.015. CCDC 1469533, 1469534, 1469535, 1469536, and 1469537 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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