JOC Article

Preparation of Six Isomeric Bis-acylporphyrins with Chromophores Reaching the Near-Infrared via Intramolecular Friedel−Crafts Reaction

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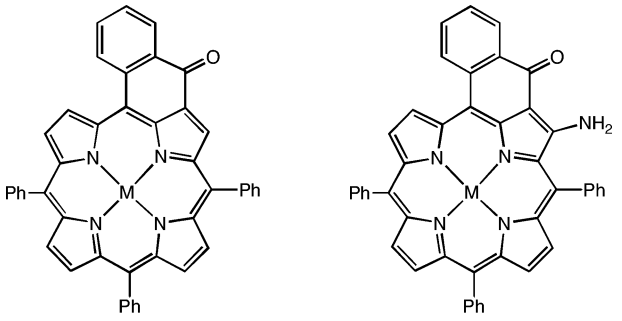
We describe the preparation of six diketones based on the frameworks of five bis-naphthoporphyrins and one perinaphthoporphyrin. All diketones derive from *meso*-tetraarylporphyrins having incorporated two carbonyl groups, each one connected to one β-pyrrole carbon and one ortho carbon atom from a *meso*-aryl group. These compounds were all produced in good yield by intramolecular Friedel−Crafts acylation, either from porphyrins *meso*-substituted by *o*-carboxyphenyl or *o,o′*-dicarboxyphenyl substituents or from porphyrins bearing carboxy groups attached to the pyrrolic β-positions. Although the former reaction does not show significant regioselectivity when run on nickel complexes, the opposite is true for the corresponding free bases. All diketones show a spectacular bathochromic shift of the UV−vis absorption, the longest wavelength bands absorbing in the 700−825 nm range. Two compounds were structurally characterized by X-ray diffraction. In the case of the diketone, whose carbonyl groups are attached to vicinal pyrrolic β-positions, a significant intermolecular interaction between the two carbonyl groups and an aromatic hydrogen atom was detected.

Introduction

The tetrapyrrolic chromophores, found in many natural photosynthetic systems, have also been used by synthetic chemists as starting compounds to build up molecules possessing extended π-conjugation.[1] These molecules are promising for potential applications in photodynamic therapy or as models for the photosynthetic reaction centers and antenna arrays. In the field of material science, improvement of the photochemical or electrochemical properties might lead to new molecular materials.

For the widely used *meso*-tetraarylporphyrins, the extension of the chromophore can be easily obtained by fusing one pyrrole and a neighboring aryl group with a keto function, thus leading to the so-called oxonaphthoporphyrins **1** or **2** (Chart 1).[2−4] This addition of two unsaturated rings in the plane of the porphyrin and the corresponding extension of the conjugation induce interesting optical properties: the nickel complex of an oxonaphthoporphyrin like **2** shows absorption as far as 650 nm, approximatively 100 nm longer wavelength than simple nickel porphyrins. Performing this kind of ring fusion twice was therefore expected to lead to further improvement of the optical properties of the porphyrin macrocycles. To our knowledge, only two examples of porphyrins *meso*+β fused with two conjugated rings have

CHART 1. Structure of Oxonaphthoporphyrins (1 and 2) and the Corresponding Enaminoketones (3 and 4)



1 : M = H_2 **3** : M = H_2

2 : M = Ni **4** : M = Ni

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(3) Callot, H. J.; Schaeffer, E.; Cromer, R.; Metz, F. *Tetrahedron* **1990**, *46*, 5253.

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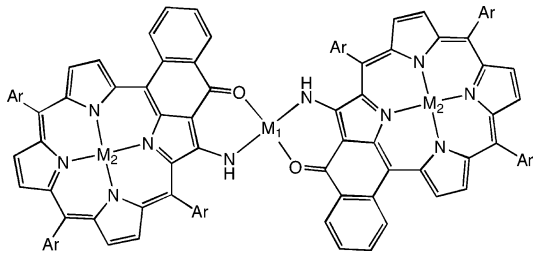
CHART 2. Dimers Obtained by Linking Two Enaminoketoporphyrins by Metal Ions



been obtained so far.[5,6] Both compounds have one pyrrole connected with the two adjacent phenyl groups either by five- or six-membered rings, but the extension of the conjugated system only produced moderate modifications of the electronic spectra.

On the other hand, we have demonstrated[7,8] that enaminoketoporphyrins such as **3** or **4**, obtained from the corresponding ketones by amination, could be used as chelating ligands for metal ions. Assembling two such molecules around a metal ion leads to a dimeric porphyrin. These dimers (Chart 2) show an extension of the chromophore and the splitting of the electrochemical waves, thus demonstrating that the metal ion connection has brought significant interactions between the two porphyrins in the ground state.

Bis-enaminoketones would allow the complexation of two metals at the periphery of one porphyrin ring and to build higher oligomers. It was thus useful to carry out the synthesis of porphyrins bearing two peripheral fused benzocyclohexenone fragments.[9]

The classical method for preparing such ketones, acid-catalyzed condensation of a β-formyl group onto a *meso*-aryl ring, is a very efficient cyclization procedure, giving a 1:1 mixture of the ketone and reduced species in ca. 90% yield. It suffers from several drawbacks when extended to higher homologues: the formylation produces several di- or polyaldehydes[10] and the subsequent cyclization should lead to complex mixtures of diketones, and monoketones, along with numerous reduced species. To avoid these difficulties, we had to develop synthetic routes based on a different reaction sequence, and we selected the Friedel−Crafts acylation. This reaction has been already illustrated in the polyalkylporphyrin series.[11,12] Several ketocycloalkanoporphyrins were prepared by intramolecular cyclization of functionalized side chains,[13] but simple Friedel−Crafts acylation of porphyrins was little explored.[14] Similar chemistry of *meso*-tetraarylporphyrins was virtually unknown until recently.[15] An additional difficulty arises when one wishes to obtain both free bases and metal complexes of the target porphyrins, since Friedel−Crafts chemistry is only compatible with a limited set of stable metal complexes. The demetalation of these complexes may also interfere with the survival of the new functional groups.

There are six possible diketones illustrated by structures **5**−**10** (Chart 3), three of them (**5**−**7**) with the carbonyl groups attached to vicinal *meso*-phenyl rings, two (**8** and **9**) with the carbonyl groups attached to opposite *meso*-phenyl rings, and one (**10**) with the two carbonyl groups attached to the same *meso*-phenyl ring. Out of the six possible diketones, five (illustrated by **5**, **6**, **8**, **9**, and **10**) represent potential starting materials for the required bis-enaminoketones, while the last one (**7**) shows a potentially interesting relationship between the two very close carbonyl groups.

In this paper, we describe the preparation and characterization of all six porphyrin diketone frameworks, as nickel complexes, as well as various attempts to prepare the corresponding free bases. We also demonstrate that several routes leading to these ketones are available, taking advantage of performing the acylation step either from *meso*-aryl groups to the porphyrin ring, but also from the porphyrin ring to the aryl groups. We present also the X-ray structures of two diketones and the electronic spectra of these compounds, demonstrating that, in these cases, the extension of the aromatic system leads to major bathochromic shifts.

Results and Discussion

Synthesis of Ketones from Porphyrin *meso*-Benzoates (Scheme 1). Condensation of *o*-carbomethoxybenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde, and pyrrole under Lindsey's conditions[16] gave a mixture of all possible esters. Diesters **11** and **12** are both present as $\alpha\alpha$ and $\alpha\beta$ atropisomers and were chromatographically isolated and transformed into the nickel complexes by reaction with nickel acetylacetonate in refluxing toluene. These diesters were hydrolyzed with LiOH in water−dioxane solution. The crude lithium salts were then converted into the acid chlorides (oxalyl chloride in benzene) and, without purification, cyclized in benzene using $SnCl_4$ as Lewis acid. The resulting nickel complexes of diketones **5** (24%), **6** (18%), and **7** (44%) (prepared from the 5,10 isomer; total yield 86%) as well as **8** (36%) and **9** (40%) (prepared from the 5,15 isomer; total yield 76%) were separated chromatographically.

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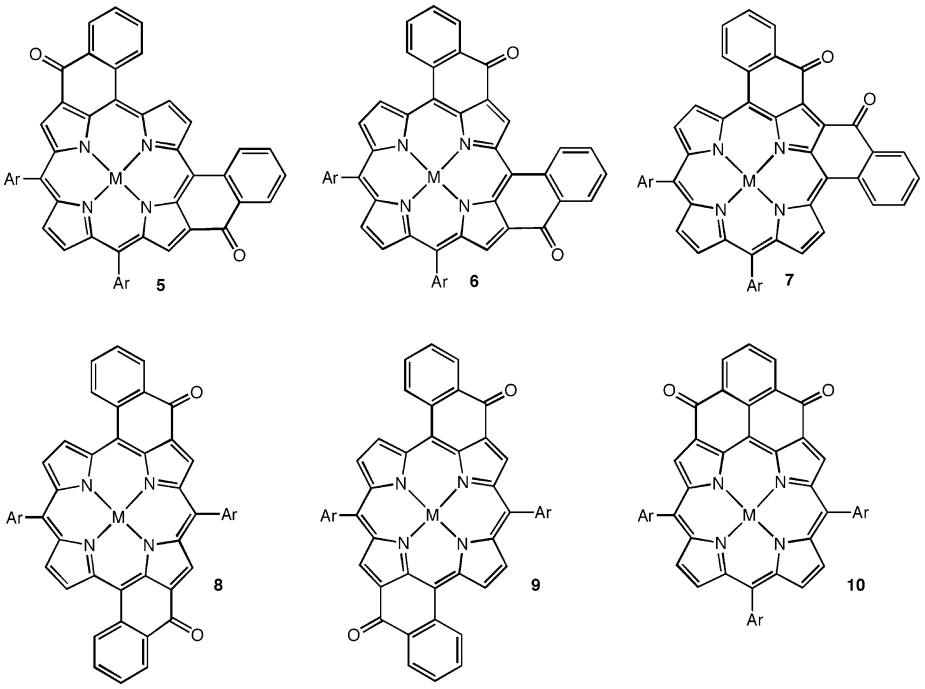
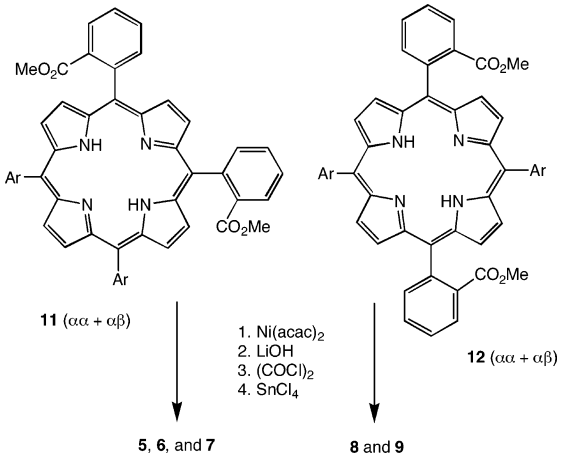
CHART 3. Structure of the Six Porphyrin Diketones 5−10



SCHEME 1. General Route to Diketones 5−9 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl)



At this stage, it should be noted that, while **5**, **6**, **8**, and **9** were eluted from silica gel with hexane−CH_2Cl_2 mixtures, the vicinal diketone **7** was very strongly adsorbed and required AcOEt + 0.1% AcOH.

The same reaction sequence was applied to porphyrins with other *meso*-aryl groups. In particular, crystals suitable for an X-ray diffraction study of **8** could be obtained with 2,6-dichlorophenyl as *meso*-aryl group (M = Ni, see below for structural data).

Synthesis of Mono- and Diketones from *β*-Cyanoporphyrins. The second route requires that carboxylic acids should be located at *β*-pyrrolic positions. They can be prepared from *β*-cyanoporphyrins which are available via bromination[17,18] of porphyrin free bases followed by reaction with cuprous cyanide.[17,19] When run without isolating the bromoporphyrins, but taking advantage of the ease of separation of the polycyanoporphyrins, this route leads efficiently to the mono- to tetracyano-*meso*-tetraarylporphyrins substituted on two opposite pyrroles.

The feasibility of this route to porphyrin ketones was tested from monocyano-H_2TPP (TPP = anion of *meso*-tetraphenylporphyrin) (Scheme 2). This compound was obtained as the copper complex **13** (Ar = phenyl) when bromoporphyrin free bases were treated with cuprous cyanide. There is no need to demetalate the complex, because its hydrolysis in AcOH + 48% aqueous HBr gave quantitatively acid **14** (Ar = phenyl) as the free base. The crude acid was then treated in the usual way (metalation with nickel, followed by treatment with oxalyl chloride and $SnCl_4$) to yield the monoketone **1** (90% from **13**), confirming that both routes are available.

Alternatively, and in order to test different conditions, possibly compatible with acid-sensitive complexing metals, the cyclization of the corresponding mixed anhydride was tested. The nickel complex of acid **14** was treated with triethylamine and ethyl chloroformate. The crude mixed anhydride was cyclized either with BF_3 etherate or zinc chloride to yield ketone **1** (M = Ni, Ar = phenyl; 32%) (Scheme 2).

Diketones **5** and **9** are the only isomers accessible from *β*-dicyanoporphyrins, since due to the regioselectivity of the bromination reaction,[18] only two dibromoporphyrins (2,12 and 2,13 isomers) are produced. The reaction sequence was run on the mixture of the two dicyanoporphyrins **15** and **16** (*meso*-phenyl series), since we observed that the separation was easier to perform at the last step. Hydrolysis and metalation gave the nickel diacids, which were then treated with oxalyl chloride and $SnCl_4$. The crude mixture of diketones was then sepa-

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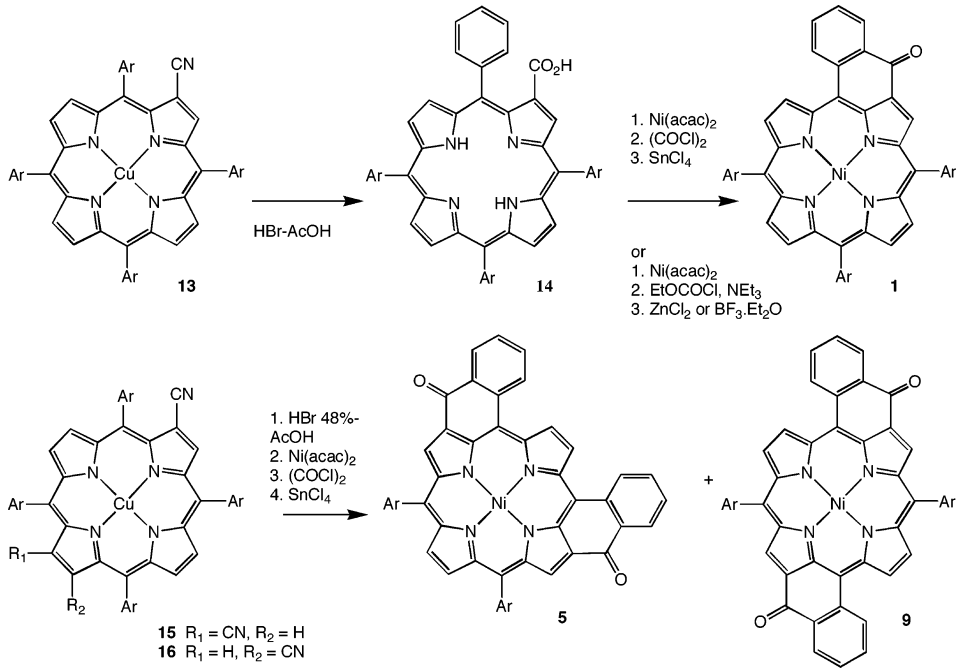
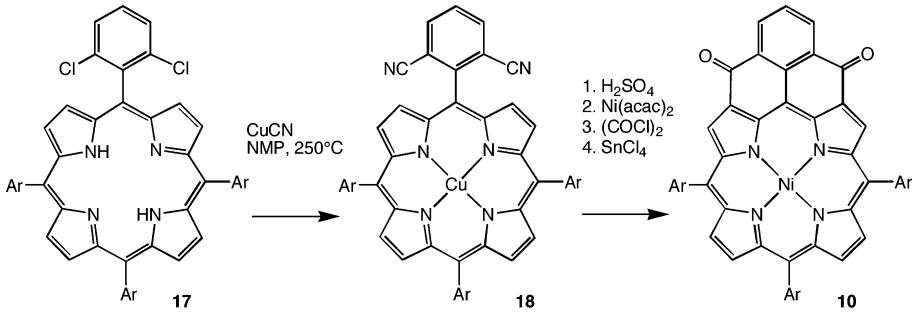
(19) Jaquinod, L.; Khoury, R. G.; Shen, K. M.; Smith, K. M. *Tetrahedron* **1999**, *55*, 13151.

SCHEME 2. Synthesis of Mono- and Diketones from *β*-Cyanoporphyrins (Ar = Phenyl)



SCHEME 3



rated by fractional crystallization and chromatography on silica gel to give **5** (M = Ni, Ar = phenyl; 27%) and **9** (M = Ni, Ar = phenyl; 30%).

Preparation of Diketone 10 (Scheme 3). Since no simple route to the appropriate *β*-dicyanoporphyrin (2,18 isomer) was available, we carried out the preparation of **10** via the *meso*-aryl to porphyrin cyclization. A reaction sequence similar to one described in the literature[20] was followed starting with *meso*-2,6-dichlorophenyl substituted porphyrin **17** to introduce carboxylic acids via cyano groups and hydrolysis. Porphyrin **17** was obtained in 20% yield by reacting 2,6-dichlorobenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde, and pyrrole. The cyanation reaction was carried out in 51% yield by reacting **17** with cuprous cyanide in *N*-methylpyrrolidinone at 250 °C in a sealed tube. Hydrolysis of the cyano groups and simultaneous demetalation of **18** in aqueous sulfuric acid, metalation with nickel (II), treatment with oxalyl chloride, and a Friedel−Crafts reaction gave diketone **10** (37% from copper dicyanoporphyrin **18**).

Synthesis of Diketone Free Bases. The general method for demetalating porphyrins, treatment with a strong acid, proved to be inefficient with the nickel diketones. Even in pure sulfuric acid or methanesulfonic acid, most starting material was recovered unchanged, while under more drastic conditions (hot acids), decomposition occurred. This lack of reactivity of the nitrogen atoms is best explained by the protonation of both carbonyl groups, which will inhibit any further protonation of the porphyrin. At this stage, there remained two possibilities: either to cyclize a carboxylic acid derivative as the free base porphyrin or to protect the porphyrin core with an acid-sensitive metal, like zinc, and find nonacidic cyclization conditions.

Preliminary tests on the zinc complex of acid **14** derivatives failed: attempted cyclization of the mixed anhydride with zinc chloride did not give ketone **1**. The direct reaction of this acid with zinc chloride (which also metalated the porphyrin ring) in refluxing chlorobenzene (at lower temperatures, no reaction occurred) only gave traces of ketonic material accompanied by extensive decarboxylation. However, under similar conditions, the corresponding nickel complex **14** (M = Ni) showed that the direct cyclization to ketone **1** (M = Ni, Ar = phenyl) occurred albeit in low yield (15% cyclized material vs 57% decarboxylation).

(20) Nakagawa, H.; Nagano, T.; Higuchi, T. *Org. Lett*. **2001**, *3*, 1805.

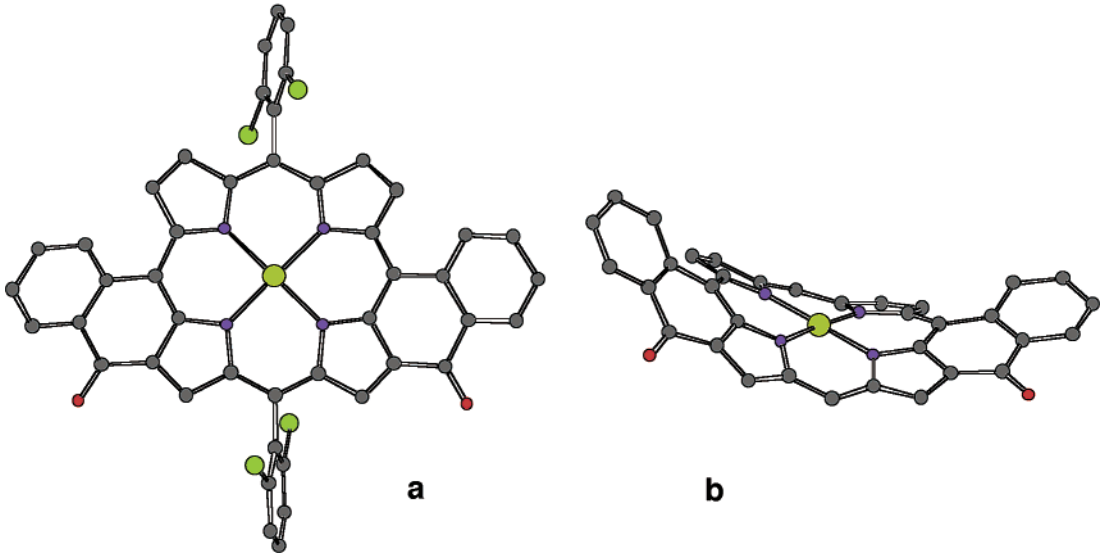
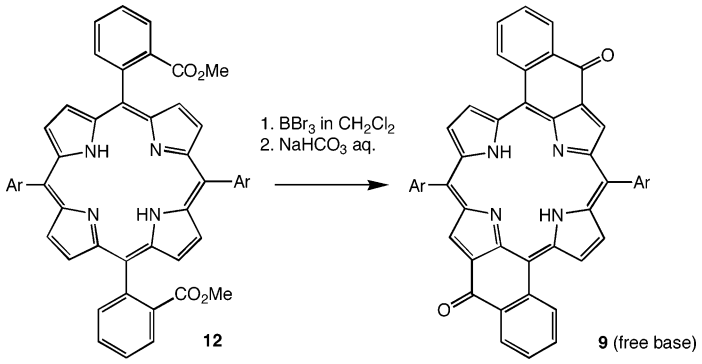


FIGURE 1. Two views of diketone **8** (Ar = 2,6-Cl_2Ph): (a) all hydrogen atoms omitted for clarity; (b) both *meso*-phenyl and all hydrogen atoms omitted for clarity).

SCHEME 4. Preparation of Diketone 9 as Free Base (Ar = 3,5-Di-*tert*-butylphenyl)



The direct cyclization of an appropriately substituted free base porphyrins was finally carried out under the conditions used by several groups[21,22] to build rings fused to pyrroles (Scheme 4). The reaction was first tested with monoesters and then applied to diesters **11** and **12**. Diester **11**, as free base, was treated with excess boron tribromide in CH_2Cl_2 (1 M) and the reaction mixture hydrolyzed under basic conditions. Diketone **6** (free base, Ar = 3,5-di-*tert*-butylphenyl), but not the other possible isomers **5** and **7**, was obtained in moderate yield (11%). Under the same conditions, diester **12** produced only diketone **9** (free base, Ar = 3,5-di-*tert*-butylphenyl) in 20% yield. The remaining porphyrinic material mostly consists of acids arising from the esters and monocyclized compounds. This reaction shows a high selectivity toward only one diketone in each series. We suggest that, in the presence of excess BBr_3, a boron complex forms rapidly. Since all known porphyrin boron complexes involve two boron atoms and thus lack the high symmetry of most porphyrin metal derivatives,[23] the pyrrolic carbon atoms are no longer equivalent and should show different reactivities. The carbonyl oxygen−boron bonds, either in the starting material (ester/central or external boron interaction) or in the monocyclized intermediate (same interactions or ketone/boron bond) are also expected to polarize the π-system and to exert additional effects on the selectivity of the acylation reaction.

Structural Data for Diketones 7 and 8. Single crystals suitable for X-ray studies could be grown for diketones **7** (M = Ni, Ar = 3,5-di-*tert*-butylphenyl) and **8** (M = Ni, Ar = 2,6-dichlorophenyl). However, due to disorder observed for the *tert*-butyl groups and for the solvents included in the unit cell, the quality of the structural data for diketone **7** is rather low. Both porphyrins are saddle-shaped as shown by the angles determined by nickel and the opposite *meso* carbons: about 154 and 159° for **7** (C5−Ni−C15 and C10−Ni−C20) and 158.3 and 158.4° for **8** respectively (C5−Ni−C15 and C10−Ni−C20). However, due to the relative positions of the carbonyl groups, this similar geometry induces a very different relationship between these groups: in **8** carbonyl groups are almost symmetrical relative to a plane perpendicular to the porphyrin (see Figure 1), while in **7** there are placed at one end of a flattened helix (see Figure 2). In both compounds, the coordination geometry of the

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(22) Sayah, B.; Pelloux-Léon, N.; Vallée, Y. *J. Org. Chem.* **2000**, *65*, 2824.
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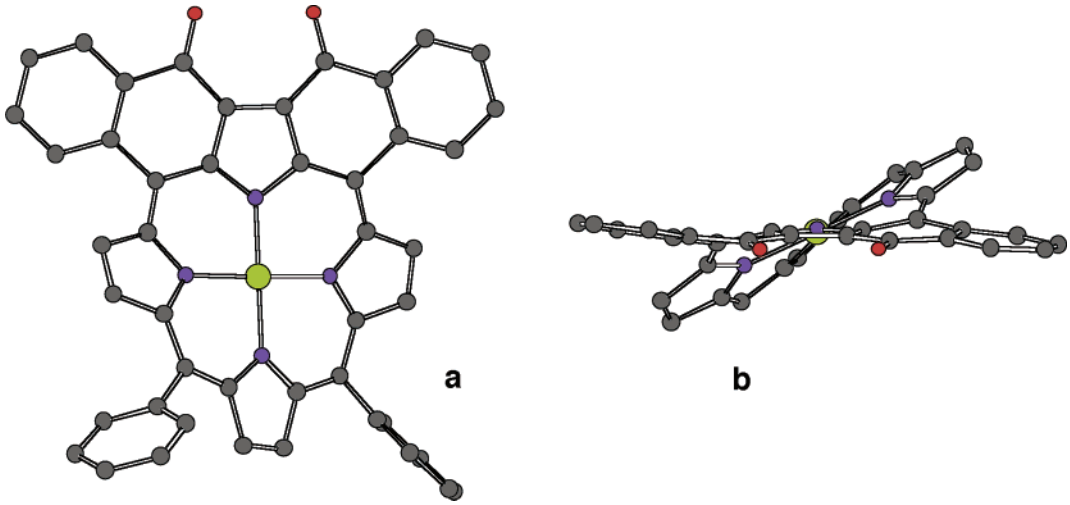

FIGURE 2. Two views of diketone **7** (Ar = 3,5-*t*-Bu_2Ph): (a) *t*-Bu groups and all hydrogen atoms omitted for clarity; (b) both *meso*-aryl and all hydrogen atoms omitted for clarity).

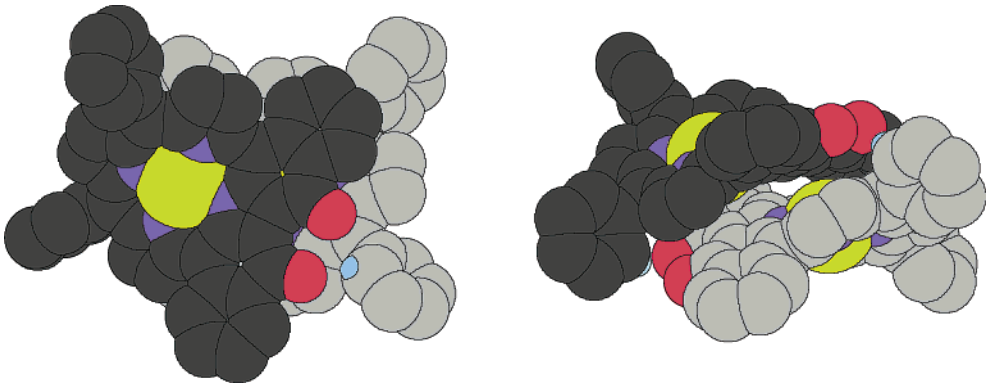

FIGURE 3. Two views (CPK representation) of the two independent molecules of diketone **7** (Ar = 3,5-*t*-Bu_2Ph) (*t*-Bu groups and all hydrogen atoms except the two involved in hydrogen bonding omitted for clarity).

nickel atoms is almost perfectly square planar, with the Ni−N bonds averaging 1.9 Å.

The formation of the additional six-membered ring induces a close contact between one pyrrolic H and one phenyl H (2.14 or 2.17 Å). It should be noted that, while in **8** the β,β' bonds are slightly longer when a carbonyl is bound to them (1.359 and 1.364 Å, vs 1.341 and 1.326 Å), this difference is notably larger in **7** where the two carbonyl groups are vicinal (1.39−1.40 Å vs 1.32−1.35 Å).

Diketone **7** is found as a pair of stacked independent porphyrins in the unit cell (see Figure 3). Very short contacts, as low as 3.25 Å, demonstrate the interaction between the two aromatic π-electronic systems. The two oxygen atoms of the diketone carbonyl functions are extremely close to each other (2.87 and 2.89 Å). This close proximity explains the very high polarity of the molecule, most probably due to the ease of protonation, experienced during the chromatographic separation (see the Experimental Section). This geometry is reminiscent of the one found in the so-called proton sponges, where two nitrogen atoms, localized at positions 1 and 8 of a naphthalene are maintained in close proximity, thus increasing their basicity. In the case of diketone **7**, the molecule can be protonated quantitatively by adding a relatively weak acid like benzene sulfonic acid (pK_a = 0.7), whereas protonation of ketones requires generally much stronger acids. The particularity of this geometric arrangement has also consequences in the solid state. Each diketone is found oriented toward one *meso*-phenyl C−H belonging to the other porphyrin with oxygen to hydrogen distances in the range of 2.38 to 2.69 Å. This is in very close agreement with the average value (2.55 Å) found in the litterature for the hydrogen bond involving an oxygen and a hydrogen bound to an sp^2 carbon.[24]

Electronic Spectra of Diketones 5−10. The cyclization via the ketofunctionality of one (for **10**) or two *meso*-aryl groups of the nickel porphyrin has a very large effect on the electronic spectra of the six diketoporphyrins. It is difficult to fully describe the localization and attribution of all bands in these spectra without theoretical calculations.[25]

However, two general comments can be made: (1) The addition of unsaturated rings fused to the core of the porphyrin leads to an extension of the conjugated system, thus leading to a bathochromic shift of all bands. (2) fusing additional rings leads to large deformations of the porphyrin core structure as shown, in our case, by the X-ray structures of diketones **7** and **8**. In general, these

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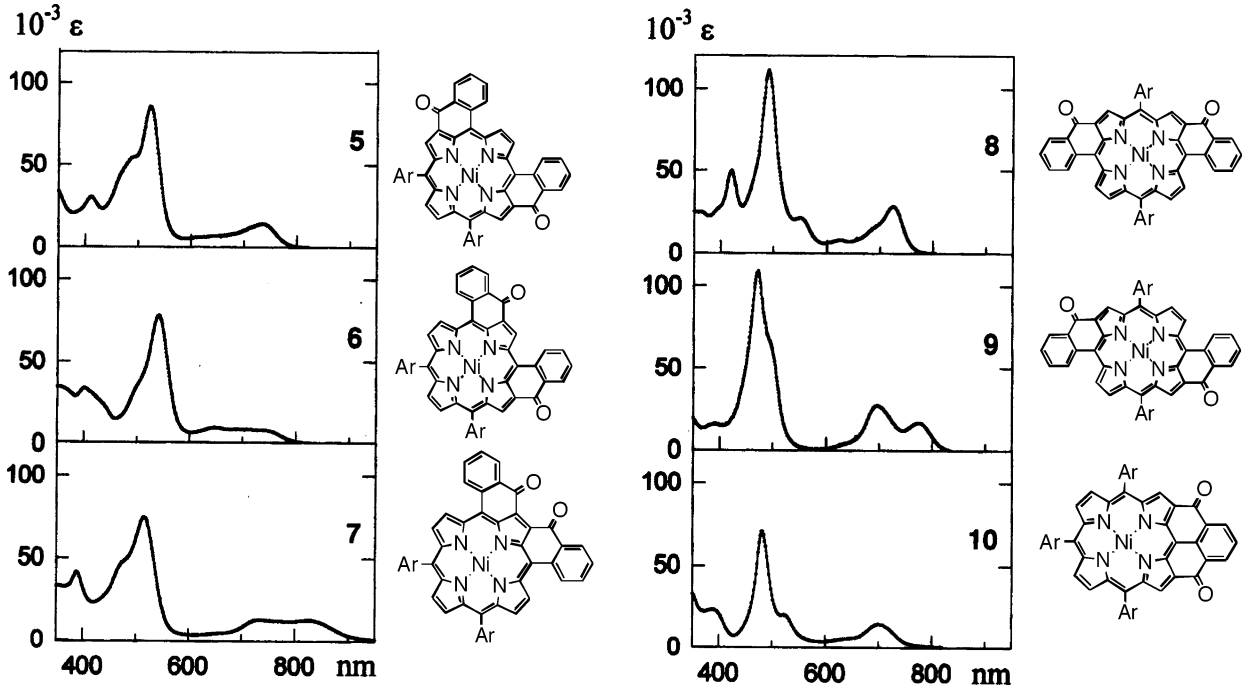

FIGURE 4. Electronic spectra of porphyrins **5**−**10** in dichloromethane.

deformations are known to induce bathochromic shifts in the electronic spectra of porphyrins.[26]

The electronic spectra and the electrochemical behavior of nickel porphyrins depend strongly on electronic and structural effects introduced by substituents at the *meso* or the *β*-pyrrolic positions. Recently, a systematic study of 29 nickel porphyrins was reported.[27] In these examples, the Soret bands were observed between 406 and 455 nm and the Q-bands between 525 and 613 nm. For the diketoporphyrins reported in this study, forcing the *meso*-aryl groups in the plane of the porphyrin by the sp^2 carbonyl bridge leads to much larger effects. The Soret bands are, respectively, seen at 524, 540, 516, 490, 472, and 482 nm for nickel porphyrins **5**−**10** (see Figure 4). The loss of symmetry leads to a splitting of the Soret bands (as a consequence, we could observe a widening of these bands or shoulders in some cases) and, thus, to a decrease of the intensity, compared to more symmetrical nickel porphyrins. The bathochromic shifts are even more impressive for the Q-bands. All diketoporphyrins present strong absorption bands between 700 and 800 nm. For porphyrin **7**, the lowest energy bands (700−900 nm) reach the near infrared region. These absorbances are quite unusual for nonreduced porphyrins: 700 or 800 nm are typical wavelength values found for dihydroporphyrins (chlorins) or tetrahydroporphyrins (bacteriochlorins).

Conclusion

The synthesis of the six diketones was carried out successfully. The intramolecular Friedel−Crafts reaction proved to be a method of choice to obtain the nickel complexes and high conversion was obtained starting from the appropriate precursors, either esters or cyano derivatives. The direct cyclization to porphyrin free bases was less satisfactory. However, it illustrated the high sensitivity of the regioselectivity of the reaction to the nature of the complexing ions. All diketones show visible absorption bands at very long wavelength (up to 826 nm), as compared to simple porphyrins or monoketones. All *β*-unsubstituted ketones are currently used as precursors to bis-enaminoketones, the building blocks for metal ion connected porphyrin oligomers.[9]

Experimental Section

Esters 11 and 12. To a degassed solution of pyrrole (1.34 g, 20 mmol), 2-carbomethoxybenzaldehyde (1.64 g, 10 mmol) and 3,5-di-*tert*-butylbenzaldehyde (2.18 g, 10 mmol) in 750 mL of CH_2Cl_2 was added $BF_3{\cdot}Et_2O$ (0.4 mL, 3.15 mmol). After 3 h of stirring at room temperature, in the dark and under argon, chloranil (3 g, 12 mmol) was added and the solution heated under reflux for 1 h. The cooled solution was passed through a short pad of alumina and the solvent evaporated to dryness. Chromatography (silica gel, 500 mL, hexane to CH_2Cl_2) afforded in the order of elution tetra(3,5-di-*tert*-butylphenyl)-porphyrin (173 mg), tris(3,5-di-*tert*-butylphenyl)(*o*-carbomethoxyphenyl)porphyrin (487 mg), **12** (α*β* atropisomer) (111 mg), **11** (α*β*) (190 mg), **12** (αα) (107 mg), **11** (αα) (299 mg), and a mixture of the atropisomers of the tri- and tetraesters (not isolated).

12 (α,*β*). ^{1}H NMR: δ = 8.83 (4H, d, J = 4.8 Hz, pyrrole), 8.63 (4H, d, J = 4.8 Hz, pyrrole), 8.06 (4H, d, J = 1.8 Hz, Ar-*o*-H), 7.77 (2H, t, J = 1.8 Hz, Ar-*p*-H), 8.38 (2H, dd, J = 7.7, 1.5 Hz, benzoate), 8.15 (2H, dd, J = 7, 1.5 Hz, benzoate), 7.80−7.88 (4H, m, benzoate), 2.80 (6H, s, OCH_3), 1.52 (36H, s, *t*-Bu), −2.55 (2H, s, NH).

11 (α,*β*). ^{1}H NMR: δ = 8.86 (2H, s, pyrrole), 8.82 (2H, d, J = 4.8 Hz, pyrrole), 8.63 (2H, d, J = 4.8 Hz, pyrrole), 8.60 (2H, s, pyrrole), 8.12 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 7.99 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 7.77 (2H, t, J = 1.8 Hz, Ar-*p*-H), 8.36 (2H, dd, J = 7.2, 1.5 Hz, benzoate), 8.20 (2H, dd, J = 7.0,

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1.5 Hz, benzoate), 7.80−7.88 (4H, m, benzoate), 2.74 (6H, s, OCH_3), 1.53 (18H, s, *t*-Bu), 1.50 (18H, s, *t*-Bu), −2.55 (2H, s, NH).

12 (α,α). ^{1}H NMR: δ = 8.82 (2H, d, J = 4.8 Hz, pyrrole), 8.62 (2H, d, J = 4.8 Hz, pyrrole), 8.16 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 7.97 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 7.77 (2H, t, J = 1.8 Hz, Ar-*p*-H), 8.39 (2H, dd, J = 7.5, 1.5 Hz, benzoate), 8.16 (2H, dd, J = 7.0, 1.5 Hz, benzoate), 7.80−7.88 (4H, m, benzoate), 2.87 (6H, s, OCH_3), 1.54 (18H, s, *t*-Bu), 1.49 (18H, s, *t*-Bu), −2.54 (2H, s, NH).

11 (α,α). ^{1}H NMR: δ = 8.86 (2H, s, pyrrole), 8.83 (2H, d, J = 4.8 Hz, pyrrole), 8.66 (2H, d, J = 4.8 Hz, pyrrole), 8.59 (2H, s, pyrrole), 8.07 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 8.04 (2H, dd, J = 1.8, 1.8 Hz, Ar-*o*-H), 7.78 (2H, t, J = 1.8 Hz, Ar-*p*-H), 8.37 (2H, dd, J = 7.3, 1.5 Hz, benzoate), 8.18 (2H, dd, J = 7.0, 1.5 Hz, benzoate), 7.80−7.88 (4H, m, benzoate), 2.67 (6H, s, OCH_3), 1.52 (18H, s, *t*-Bu), 1.51 (18H, s, *t*-Bu), −2.55 (2H, s, NH).

The two atropisomers of each diester were mixed, metalated quantitatively with Ni(acac)$_2$ in refluxing toluene, and crystallized from CH_2Cl_2/MeOH.

Diketones 8 and 9 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). A solution of the nickel complex of diester **12** (96 mg, 95 μmoles) and LiOH·H_2O (100 mg, 2.48 mmol) in dioxane/water (100 mL, 4:1) was heated at 100 °C and stirred under argon during 24 h. The solvents were evaporated, and the solid residue was dried under vacuum. To this residue were added benzene (100 mL) and oxalyl chloride (5 mL, 57 mmol), and the solution was heated during 3 h at 50 °C. The solvents were partly evaporated (10 mL, to eliminate excess oxalyl chloride), and $SnCl_4$ (1 mL, 8.5 mmol) was added. After 30 min, CH_2Cl_2 (200 mL) was added and the solution neutralized with aqueous NaOH. The organic phase was washed with water (5 × 1L) and dried with Na_2SO_4. Chromatography (silica gel, 300 mL, hexane to CH_2Cl_2) and crystallization from CH_2Cl_2/MeOH afforded the brown diketone **8** (32 mg, 36%) and the yellow diketone **9** (36 mg, 40%).

Diketone 8 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR (318 K): δ = 9.01 (2H, d, J = 5.1 Hz, pyrrole), 8.94 (2H, s, pyrrole), 8.41 (2H, d, J = 5.1 Hz, pyrrole), 7.75 (1H, t, J = 1.8 Hz, Ar-*p*-H), 7.73 (1H, t, J = 1.8 Hz, Ar-*p*-H), 7.70 (2H, d, J = 1.8 Hz, Ar-*o*-H), 7.65 (2H, d, J = 1.8 Hz, Ar-*o*-H), 8.46 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.96 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.70 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.50 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 1.47 (18H, s, *t*-Bu), 1.45 (18H, s, *t*-Bu). ^{13}C NMR: δ = 182.1 (CO). UV−vis: λ_{max}(nm) = 420 (ϵ = 51 000), 490 (111 000), 550 (21 600), 726 (28 200). Anal. Calcd for $C_{62}H_{56}N_4O_2Ni$·0.5H_2O: C, 77.83; H, 6.00; N, 5.86. Found: C, 77.84; H, 5.84; N, 5.68.

Diketone 9 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR (318 K): δ = 8.99 (2H, d, J = 5 Hz, pyrrole), 8.88 (2H, s, pyrrole), 8.52 (2H, d, J = 5 Hz, pyrrole), 7.75 (2H, t, J = 1.8 Hz, Ar-*p*-H), 7.70 (4H, broad d, J = 1.8 Hz, Ar-*o*-H), 8.43 (2H, dd, J = 7.5, 1 Hz, cyclized phenyl), 8.01 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.70 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.48 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 1.47 (36H, s, *t*-Bu). ^{13}C NMR: δ = 181.4 (CO). UV−vis: λ_{max}(nm) = 472 (ϵ = 109 000), 698 (27 400), 776 (17 300). Anal. Calcd for $C_{62}H_{56}N_4O_2Ni$: C, 78.57; H, 5.96; N, 5.91. Found: C, 78.21; H, 5.81; N, 5.83.

Diketones 5, 6, and 7 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). These diketones were prepared from **11** following the same procedure in 18, 24, and 44% respectively (see the Supporting Information).

Diketone 5 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR: δ = 9.05 (2H, s, pyrrole), 8.94 (2H, s, pyrrole), 8.28 (2H, s, pyrrole), 7.70 (2H, t, J = 1.8 Hz, Ar-*p*-H), 7.66 (4H, d, J = 1.8 Hz, Ar-*o*-H), 8.40 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.67 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.61 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.44 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 1.45 (36H, s, *t*-Bu). ^{13}C NMR: δ = 182.3 (CO). UV−vis: λ_{max}(nm) = 412 (ϵ = 30 100), 480 (55 000, sh), 524 (85 000), 736 (14 000). Anal. Calcd for $C_{62}H_{56}N_4O_2Ni$: C, 78.57; H, 5.96; N, 5.91. Found: C, 78.24; H, 5.92; N, 5.77.

Diketone 6 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR: δ = 9.34 (1H, broad s, pyrrole), 8.90 (1H, d, J = 5 Hz, pyrrole), 8.51 (1H, d, J = 5 Hz, pyrrole), 8.87 (1H, s, pyrrole), 8.34 (1H, d, J = 5 Hz, pyrrole), 8.17 (1H, d, J = 5 Hz, pyrrole), 7.70−7.74 (6H, m, Ar-*o*-H and Ar-*p*-H), 8.38 (1H, dd, J = 7.6, 1 Hz, cyclized phenyl), 8.28 (1H, dd, J = 7.6, 1 Hz, cyclized phenyl), 7.80 (1H, dd, J = 7.6, 1 Hz, cyclized phenyl), 7.75 (1H, dd, J = 7.6, 1 Hz, cyclized phenyl), 7.64 (1H, ddd, J = 7.6, 7.5, 1 Hz, cyclized phenyl), 7.61 (1H, ddd, J = 7.6, 7.5, 1 Hz, cyclized phenyl), 7.45 (1H, ddd, J = 7.6, 7.5, 1 Hz, cyclized phenyl), 7.39 (1H, ddd, J = 7.6, 7.5, 1 Hz, cyclized phenyl), 1.47 (18H, s, *t*-Bu), 1.46 (18H, s, *t*-Bu). ^{13}C NMR: δ = 181.6 and 181.9 (CO). UV−vis: λ_{max}(nm) = 402 (ϵ = 36 000), 500 (38 000, sh), 540 (78 000), 646 (10 500), 750 (9000, sh). Anal. Calcd for $C_{62}H_{56}N_4O_2Ni$·H_2O: C, 77.10; H, 6.05; N, 5.80. Found: C, 77.35; H, 5.78; N, 5.67.

Diketone 7 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR ($CDCl_3$, 318 K): δ = 8.92 (2H, d, J = 5.1 Hz, pyrrole), 8.34 (2H, d, J = 5.1 Hz, pyrrole), 8.14 (2H, s, pyrrole), 7.69 (2H, t, J = 1.8 Hz, Ar-*p*-H), 7.66 (4H, d, J = 1.8 Hz, Ar-*o*-H), 8.51 (2H, dd, J = 7.7, 1 Hz, cyclized phenyl), 7.76 (2H, dd, J = 7.7, 1 Hz, cyclized phenyl), 7.61 (2H, ddd, J = 7.7, 7.2, 1 Hz, cyclized phenyl), 7.48 (2H, ddd, J = 7.7, 7.2, 1 Hz, cyclized phenyl), 1.46 (36H, s, *t*-Bu). ^{13}C NMR: δ = 179.9 (CO). UV−vis: λ_{max}(nm) = 390 (ϵ = 41 800), 480 (51 000, sh), 516 (74 800), 738 (12 000), 826 (11 700). Anal. Calcd for $C_{62}H_{56}N_4O_2Ni$: C, 78.57; H, 5.96; N, 5.91. Found: C, 78.46; H, 5.78; N, 5.67.

Nickel Complex of Ketone 1 (M = Ni, Ar = Phenyl) from Copper 2-CyanoTPP 13. A mixture of of copper 2-cyanoTPP **13** (600 mg, 0.85 mmol) in AcOH (500 mL) and aq HBr (48%, 300 mL) was heated under reflux for 4 days and then diluted with $CHCl_3$ (400 mL). This solution was washed with water until the organic phase showed a stable purple-brown color (6 to 8 washings with 400 mL water). The solution was dried (Na_2SO_4) and concentrated. Addition of hexane gave a violet powder which was dried at 100 °C (552 mg) and used as such. This crude product, nickel acetylacetonate (1 g), and DMF (400 mL) were heated under reflux for 5 min. After the solution was cooled, slow addition of 10% aq AcOH induced the crystallization of the nickel complex of acid **14**, which was filtered, washed with 10% aq AcOH, and dried at 100 °C (635 mg). ^{1}H NMR: δ = 9.06 (1H, s, pyrrole), 8.75, 8.73, 8.69, 8.68, 8.64 (1+1+1+2+1H, 5d, J = 5 Hz, pyrrole), 8−8.1 (8H, m, Ph *o*-H), 7.6−7.8 (12H, m, Ph *m*+*p*-H). Ketone **1** (M = Ni, Ar = phenyl) was then prepared either in one step, or from the acid chloride, or from a mixed anhydride.

Direct Route. The crude nickel complex of acid **14** (50 mg) and dry $ZnCl_2$ (50 mg) were stirred in refluxing 1,2-dichlorobenzene (25 mL) for 90 min. Evaporation of the solvent gave a residue which was chromatographed (silica gel, CH_2Cl_2) to give nickel *meso*-tetraphenylporphyrin (26 mg, 57% from **13**) and ketone **1** (M = Ni, 7 mg, 15% from **13**).

Acid Chloride Route. A solution of crude nickel complex of acid **14** (20 mg) in dry CH_2Cl_2 (5 mL) was treated with oxalyl chloride (0.5 mL). After 1 h, the solvant and reagent were evaporated under vacuum, and dry CH_2Cl_2 (5 mL) was added followed by $SnCl_4$ (0.1 mL). The red solution turned immediately brown. After 5 min, the reaction mixture was hydrolyzed with aq $NaHCO_3$ and dried (Na_2SO_4). Filtration through a short silica gel column and crystallization from CH_2Cl_2/MeOH gave ketone **1** (M = Ni, 17 mg, 90% from **13**).

Mixed Anhydride Route. A solution of crude nickel complex of acid **14** (50 mg) in acetone (5 mL) was treated with triethylamine (0.1 mL) and ethyl chloroformate (0.05 mL). The solution was stirred for 20 min, washed with water, dried, and evaporated. Toluene (10 mL) was added and evaporated twice to eliminate the last traces of reagents. The crude mixed anhydride was dissolved in CH_2Cl_2 (5 mL), and $ZnCl_2$ (50 mg) was added at once. After 1 h, the brown reaction mixture was

washed with aq $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated. Chromatography on silica gel (200 mL in CH_2Cl_2) gave green ketone **1** (M = Ni; 16 mg; 34% from **13**). When $ZnCl_2$ was replaced by $BF_3{\cdot}Et_2O$ the yield of ketone **1** dropped to 17%.

Diketones 5 and 9 (M = Ni, Ar = Phenyl) from Dicyanoporphyrins 15 and 16. Diketones **5** and **9** (Ar = phenyl) were prepared from **15** and **16** as above (acid chloride route) in 30 and 27%, respectively (see the Supporting Information).

***meso*-Tris(3,5-di-*tert*-butylphenyl)(2,6-dichlorophenyl)porphyrin 17.** To a solution of 3,5-di-*tert*-butylbenzaldehyde (982 mg, 4.5 mmol), 2,6-dichlorobenzaldehyde (262 mg, 1.5 mmol), and pyrrole (402 mg, 6 mmol) in CH_2Cl_2 (750 mL), kept under argon, was added $BF_3{\cdot}Et_2O$ (0.2 mL). The solution was stirred for 1.5 h, treated with chloranil (1 g), and stirred for an additional 1.5 h. The solution was filtered on alumina (150 mL). Evaporation of the solvent gave a residue which was chromatographed (silica gel; 400 mL in hexane/CH_2Cl_2 2:1). Elution with the same solvent gave a first fraction containing *meso*-tetra(3,5-di-*tert*-butylphenyl)porphyrin, followed by the required product **17**, which was crystallized from CH_2Cl_2/MeOH (160 mg; 20%). ^{1}H NMR: δ = 8.92 (6H, m, pyrrole), 8.66 (2H, d, J = 5 Hz, pyrrole), 8.07 (6H, m, di-*tert*-butylphenyl o−H), 7.70 (6H, m, remaining phenyl H), 1.54 (54H, s, *tert*-butyl), −2.6 (2H, broad signal, NH). UV−vis (as the copper complex): λ_{max}(nm) = 414 (ϵ = 403 000), 540 (22000). Anal. (as the copper complex) Calcd for $C_{68}H_{74}N_4Cl_2Cu$: C, 75.50; H, 6.89; N, 5.18. Found: C, 75.54; H, 6.92; N, 5.23.

Copper Complex of *meso*-Tris(3,5-di-*tert*-butylphenyl)-(2,6-dicyanophenyl)porphyrin 18. Porphyrin **17** (145 mg, 0.145 mmol), CuCN (230 mg, 2.5 mmol), and *N*-methylpyrrolidinone (3 mL) were sealed under vacuum in a glass tube and heated to 250 °C for 15 h. After opening of the tube, the reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with water (7 × 150 mL), dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (300 mL, hexane/CH_2Cl_2 1:1). Slow elution gave traces of starting material, an intermediate fraction (25 mg; possibly monocyanated product), followed by the copper dicyanoporphyrin **18**, crystallized from MeOH (80 mg, 51%). This product is sensitive to light and should be protected during its purification. UV−vis: λ_{max}(nm) = 422 (ϵ = 360 000), 542 (21 200). Anal. Calcd for $C_{70}H_{74}N_6Cu$: C, 79.10; H, 7.02; N, 7.91. Found: C, 78.67; H, 6.80; N, 8.01.

Nickel Complex of Diketone 10 (M = Ni, Ar = 3,5-Di-*tert*-butylphenyl). Copper complex **18** (24 mg, 0.022 mmol) was stirred in TFA/H_2SO_4 (10 mL, 1:1) until complete dissolution. To the green solution was added AcOH (15 mL), and 10 mL of the mixture was removed by boiling. To this solution were added AcOH (8 mL) and water (2 mL), and the mixture was heated under reflux for 24 h. This green solution was cooled, diluted with $CHCl_3$ (50 mL), and washed with water until the organic phase showed a stable purple-brown color. This solution was dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in DMF (20 mL) and brought to ebullition. Addition of nickel acetate (200 mg) and further boiling for 3 min gave a red solution. After cooling, slow addition of a water−acetic acid (1:1) mixture induced the precipitation of the diacid, which was filtered, thoroughly washed with water, and dried under vacuum. This product was used as such for the next step. The crude diacid (ca 20 mg) was dissolved in dry benzene (20 mL) and treated at 25 °C with oxalyl chloride (1 mL). After 2 h, the solution was evaporated to dryness under vacuum and the residue dissolved in benzene (15 mL). Upon addition of $SnCl_4$ (0.1 mL), the red solution turned rapidly brown and was stirred for 15 min. The reaction mixture was then diluted with $CHCl_3$ (100 mL), saturated aqueous $NaHCO_3$ (100 mL) was added, and the two phases were stirred vigorously for 30 min. The organic phase was decanted, washed with water (3 × 100 mL), dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (100 mL, $CHCl_3$). Elution with $CHCl_3$ gave a major pinkish-brown fraction containing diketone **10**. Evaporation of the solvent gave a brown solid which was put in suspension in hexane, filtered, and washed with hexane (10 mg, 37% as $CHCl_3$ solvate). ^{1}H NMR: δ = 9.24 (2H, s, pyrrole), 8.53 (2H, d, J = 5 Hz, pyrrole), 8.49 (2H, dd, J = 8 and 1.8 Hz, cyclized phenyl), 8, 47 (2H, d, J = 5 Hz, pyrrole), 7.83 (6H, m, di-*tert*-butylphenyl *o*-H), 7.78 (3H, m, di-*tert*-butylphenyl *p*-H), 7.51 (1H, t, J = 8 Hz, cyclized phenyl). UV−vis: λ_{max}(nm) = 348 (ϵ = 33 000), 386 (23 200), 482 (70 600), 522 (19 200), 698 (20 200). Anal. Calcd for $C_{70}H_{72}N_4O_2Ni{\cdot}CHCl_3$: C, 72.30; H, 6.24; N, 4.75. Found: C, 73.05; H, 6.17; N, 4.91. A better C figure could not be obtained.

Diketone Free Bases 6 and 9 (M = H_2, Ar = 3,5-Di-*tert*-butylphenyl). Diester **11** (96 mg, 0.1 mmol) was dissolved in a molar solution of BBr_3 in CH_2Cl_2 (6 mL, 6 mmol). After 10 h at 20 °C, the solution was treated with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. The residue was chromatographed (silica gel, 100 mL, CH_2Cl_2 to CH_2Cl_2/AcOEt 5:2). The low polarity fraction contained only one product which was crystallized in CH_2Cl_2/MeOH to give crystals of **6** (10 mg, 11%). An identical procedure was followed from diester **12** to give **9** (20%).

Diketone 6 (M = H_2, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR: δ = 9.81 (1H, s, pyrrole), 8.98 (1H, s, pyrrole), 8.98 (1H, d, J = 4.8 Hz, pyrrole), 8.51 (1H, dd, J = 7.8, 1 Hz, cyclized phenyl), 8.47 (1H, dd, J = 7.8, 1 Hz, cyclized phenyl), 8.38 (1H, d, J = 4.8 Hz, pyrrole), 8.30 (1H, d, J = 4.8 Hz, pyrrole), 8.19 (1H, dd, J = 7.8, 1 Hz, cyclized phenyl), 8.18 (1H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.87 (2H, d, J = 1.8 Hz, di-*tert*-butylphenyl *o*-H), 7.82 (2H, d, J = 1.8 Hz, di-*tert*-butylphenyl *o*-H), 7.79 (1H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.78 (1+1H, 2t, J = 1.8 Hz, di-*tert*-butylphenyl *p*-H), 7.77 (1H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.53 (1H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.48 (1H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 1.52 (18H, s, *tert*-butyl), 1.49 (18H, s, *tert*-butyl). The NH signals could not be detected. UV−vis: λ_{max}(nm) = 542 (ϵ = 89 000), 702 (13 000), 754 (12500). Anal. Calcd for $C_{62}H_{58}N_4O_2{\cdot}0.5H_2O$: C, 81.10; H, 6.70; N, 6.10. Found: C, 81.01; H, 6.30; N, 6.10.

Diketone 9 (M = H_2, Ar = 3,5-Di-*tert*-butylphenyl). ^{1}H NMR: δ = 9.12 (2H, d, J = 4.9 Hz, pyrrole), 9. 02 (2H, s, pyrrole), 8.49 (2H, d, J = 4.9 Hz, pyrrole), 8.45 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 8.23 (2H, dd, J = 7.8, 1 Hz, cyclized phenyl), 7.81 (4H, d, J = 1.7 Hz, di-*tert*-butylphenyl *o*-H), 7.78 (2H, t, J = 1.7 Hz, di-*tert*-butylphenyl *p*-H), 7.76 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 7.50 (2H, ddd, J = 7.8, 7.8, 1 Hz, cyclized phenyl), 1.53 (36H, s, *tert*-butyl). The NH signals could not be detected. UV−vis: λ_{max}(nm) = 468 (ϵ = 120 100), 504 (72 000), 622 (6300), 688 (9500), 842 (19 000). Anal. Calcd for $C_{62}H_{58}N_4O_2{\cdot}2MeOH$: C, 80.47; H, 6.96; N, 5.87. Found: C, 80.23; H, 6.68; N, 5.53.

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Note Added in Proof. A lower homologue of diketone **7** was recently described in the *seco*-porphyrin series. See: McCarthy, J. R.; Hyland, M. A.; Brückner, C. *Chem. Commun.* **2003**, 1738.

Supporting Information Available: General experimental procedures and selected synthetic procedures. Crystal data for compounds **7** and **8**. X-ray data for compounds **7** and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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