is the equilibrium constant for complex formation (cf. ref 5).

$$\left(\frac{\partial \ln (k_0/T)}{\partial T}\right)_{X_2,P} = \left(\frac{\partial \ln (k/T)}{\partial T}\right)_{X_2,P} + \left(\frac{\partial \ln K}{\partial T}\right)_{X_2,P} - 4\left(\frac{\partial \ln \sum A_i}{\partial T}\right)_{X_2,P}$$

$$\Delta H^{\ddagger} = \Delta H^* + \Delta H^\circ - 4\frac{(-M\phi L_{\mathrm{ROH}})}{\sum A_i = M} = \Delta H^* + \Delta H^\circ + 4\phi L_{\mathrm{ROH}}$$

An equivalent way to write the expression is:

$$k_{\mathrm{obsd}} = kK'\gamma_\phi^{-4}$$

$$RT \ln \gamma_\phi = \phi G^e = \phi L - T\phi S^e$$

The molecular origin of the apparent relative molal functions lies in the polymer equilibria among the alcoholic species and is shown below (see ref 1 and references therein).

The ϕL_{ROH} term is the phenomenological consequence of equilibria among all polymeric species of alcohol:

$$2A_1 = A_2;\ \Delta H^\circ_{11},\ K_{11}$$

$$A_2 + A_1 = A_3;\ \Delta H^\circ_{12},\ K_{12}$$

$$\cdots$$

$$A_i + A_j = A_{ij};\ \Delta H^\circ_{ij},\ K_{ij}$$

where all the ΔH_{ij}'s and K_{ij}'s are assumed equal. Gill and Farquhar have shown that

$$-M\phi L = K_{ij}(A_1)^2\Delta H^\circ_{ij} + 2K_{ij}(A_1)^3\Delta H^\circ_{ij} + \ldots$$

$$\mathrm{d} \ln (\textstyle\sum A_{ij})/\mathrm{d}T = \frac{\partial(\sum A_{ij})K_{ij}/\partial T}{\sum(A_{ij})} - \frac{M\phi L_2}{\sum(A_{ij})}RT^2$$

$\sum(A_{ij})$ contains $(A_1 + 2A_2 + 3A_3 + 4A_4 + \ldots)$ moles of alcohol as measured in the laboratory in terms of the simple monomeric formula. The first term represents the change in composition with T at constant equilibrium constant; that is, it reflects the change in density of the solution with temperature, which in our experiments is small and relatively constant over the temperature interval.

$$\therefore\ \Delta H^{\ddagger}_{\mathrm{app}} = \Delta H^* + \Delta H^\circ_{\mathrm{c}} + 4\phi L_{\mathrm{ROH}}$$

A similar expression can be deduced for the entropy correction.

Dimers of 5,15-Dioxoporphodimethenes with Direct Links between Methine Bridge Carbon Atoms[†]

Jürgen-Hinrich Fuhrhop,* Ehrenfried Baumgartner, and Hans Bauer

Contribution from the Institut für Organische Chemie der Freien Universität Berlin, D-1000 Berlin 33, West Germany. *Received November 3, 1980*

Abstract: Oxidation of zinc octaethylporphyrin with thallium(III) trifluoroacetate yields two dimeric 5,15-dioxoporphodimethenes with direct linkages between methine bridge carbon atoms C-10^1 and C-10^2. [Indexes 1 and 2 relate to the dioxoporphodimethene units throughout this paper.] One is the symmetric dimer in a gauche conformation; the other is an unsymmetric tautomer. Dehydrogenation of both dimers yields one product with a double bond between C-10^1 and C-10^2. This is probably the sterically most crowded tetrasubstituted olefin reported so far, and it produces a strong absorption band at 710 nm (zinc complex, 900 nm). Acetylation of monomeric and dimeric 5,15-dioxoporphodimethenes leads to a lactam, in which the methine bridge C-10 is connected with a central nitrogen atom. The reactions observed are interpreted with a reductone model for 5,15-dioxoporphodimethenes. 5-Oxo-10-hydroxyoctaethylphlorin was also isolated and characterized.

Chemical oxidation of metalloporphyrins, e.g., **1a**, leads to reactive oxyporphyrins, e.g., **1b**, in high yield.[1-5] Further oxidation occurs on the opposite methine bridge, and 5,15-dioxoporphodimethenes, e.g., **2a**,**b**, can often be obtained as stable end products.[2,3] Our interest in the chemistry of these compounds originates from the idea that they may behave as quinone analogues. We found it tempting to combine the known redox chemistry of quinones with the coordination and photochemistries of porphyrins. It particular we hoped that the keto groups could be hydrated. Irradiation of the porphodimethene chromophors should then allow some interesting photocleavages of the water adduct. The "porphoquinone" hypothesis was based on two experimental findings. (i) It was found earlier that metalloporphyrins react in a manner similar to that of benzene derivatives and that *meso*-hydroxyporphyrins have many properties in common with phenols.[4] We therefore deduced a possible chemical analogy between *p*-benzoquinone and 5,15-dioxoporphodimethenes. (ii) It was found that certain derivatives of dioxoporphodimethenes, which will be discussed in this paper, have a strong absorption band in the near infrared. These compounds were thought to be semiquinone-type dimers with a long wavelength charge-transfer band.

This paper is a very brief account of the failure of these hypotheses and a report on some faschinating new reactions of dioxoporphodimethenes. The structure elucidation of three thallium oxidation products of symmetric zinc octaethylporphyrinate (**1a**)[1-5] and their chemical reactions are described. They turned out to be comparable in complexity to the hydrogenation products of octaethylporphyrin described recently by Eschenmoser.[6] The reaction products, however, are quite different. Although we have obtained several preparations of our products in crystalline form, none of them were suitable for X-ray analysis.[7] Therefore we had to rely on spectroscopic data and

---

[†] Dedicated to Professor Georg Manecke on the occasion of his 65th anniversary.

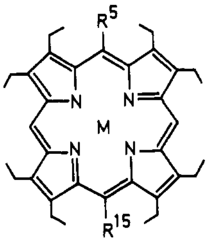
(1) Barnett, G. H.; Hudson, M. F.; McCombie, S. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 691.
(2) Barnett, G. H.; Evans, B.; Smith, K. M. *Tetrahedron* **1975**, 2711.
(3) Fuhrhop, J.-H. *Chem. Commun.* **1970**, 781.
(4) Fuhrhop, J.-H.; Besecke, S.; Subramanian, J.; Mengersen, C.; Riesner, D. *J. Am. Chem. Soc.* **1975**, *97*, 7141.
(5) Lang, F. Diplomarbeit, Braunschweig, 1976. Baumgartner, E. Dissertation, Freie Universität, Berlin, 1980.
(6) Angst, C.; Kajiwara, M.; Zass, E.; Eschenmoser, A. *Angew. Chem.* **1980**, *92*, 139. Johansen, J. E.; Angst, C.; Kratky, C.; Eschenmoser, A. *Ibid.* **1980**, *92*, 141.

0002-7863/81/1503-5854$01.25/0

on chemical interconversions to known compounds.

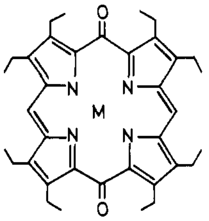
Results

Zinc octaethylporphyrin (**1a**) was oxidized in dichloromethane–tetrahydrofuran with an approximate twofold excess of TTFA. After 30 min the thallium(III) was reduced with sulfur dioxide, the zinc central ion removed with acid, and the product chromatographed on preparative TLC plates by using chloroform as eluant. Only trace amounts of octaethylporphyrin **1c** were detected at the solvent front. Five compounds eluted in the following order: 5,15-dioxoporphodimethene **2b** (R_f 0.9, 8% yield), unknown compound A (0.6, 18%), unknown compound B (0.5, 12%), oxyporphyrin **1d** (0.2, 13%), and unknown compound C (0.0, 10%). C was rechromatographed with a more polar solvent.



1

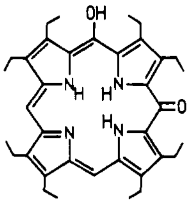
1a, $R^5 = R^{15} = H$; M = Zn
b, R^5 = OH; R^{15} = H; M = Zn
c, $R^5 = R^{15} = H$; M = 2H
d, R^5 = OH; R^{15} = H; M = 2H
e, $R^5 = R^{15} = OCOCH_3$; M = Zn
f, $R^5 = R^{15} = OCOCH_3$; M = 2H
h, $R^5 = R^{15} = OCOCF_3$; M = Zn



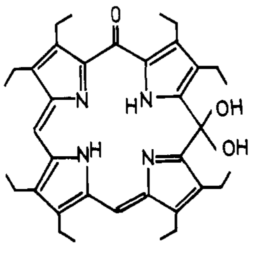
2a M = Zn
2b M = 2H

Symmetrical Dimer of Dioxoporphodimethene. Compound A (mp 289–291 °C) gave an elemental analysis which was identical with that of dioxoporphodimethene **2b**. When left standing in chloroform solution, it slowly decomposed in part to form unknown compound B and 5,15-dioxoporphodimethene **2b**. After 1 week **2b** was isolated in 40% yield. Several brown byproducts with uncharacteristic electronic spectra were detected but not further investigated. Their combined yield was estimated as less than 10%. With the isolated products *A*, *B*, and **2b** it was shown by TLC and UV/visible spectroscopy that A and B were interconvertible. They equilibrated slowly in solution. Dioxoporphodimethene **2b**, however, was stable and did not form compounds A and B. Even in the presence of thalliumacetate or sulfuric acid no decomposition of **2b** was observed within 30 min. Therefore the 5,15-dioxo compound does not show any isomerizations even under acid conditions, and we consider it highly unlikely that 5,10 hydroxy or oxo analogues such as **3a,b** could isomerize to **2b**. These structures have been proposed earlier by Smith[2] and by us[4] for the unsymmetrical thallium oxidation product.

The chemical nature of the oxygen-containing functional groups becomes evident from the ^{13}C NMR and infrared spectra. The ^{13}C NMR spectrum produces two singlets for carbonyl carbons (δ 176.88 and 174.51) as well as 16 singlets for pyrrolic carbons (δ 126.04–152.80). Doublet signals at 120.56 and 38.32 ppm may be assigned to an unsaturated and a saturated methine bridge (see below). No other signals in the range between 20 and 120 ppm were detected. This excludes any alcohol or epoxide carbon atoms. The infrared spectrum was very similar to the spectrum of dioxoporphodimethene **2b** and did not produce any extra absorption bands for OH groups. The evidence given so far (elemental analysis, conversion to **2b**, ^{13}C NMR) proves that a 5,15-dioxoporphodimethene chromophore and structures **3a,b** must be rejected for compound A.

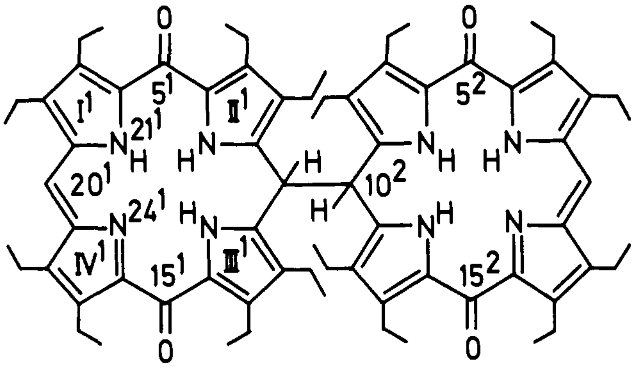


3a



3b

As mentioned above, the ^{13}C NMR spectrum indicates one unsaturated and one saturated methine carbon atom. The ^1H NMR spectrum confirms the following: two singlets for one proton each at δ 6.62 and 4.64. A gated decoupled ^{13}C NMR spectrum shows that the CH group absorbing at 4.64 ppm is connected with another CH group, since the signal at δ 38.32 is split into two doublets ($^1J_{CH} = 128.5$, $^2J_{CH} = 5.5$ Hz). Since both bridge carbon atoms 10 and 20 bear protons and no heteroatoms (elemental analysis, mass spectrum, conversion to **2b**), these results clearly indicate for compound A structure **4**, a symmetrical dimer in which both monomers are connected by a covalent bond. Any other structure with protons adjacent to a methine bridge would be nonsymmetric and lead to a splitting of the signal at 4.64 ppm into a doublet, which is not observed.



4

Several other experimental facts support this unusual structural proposal. Field desorption mass spectrometry gives a strong peak at *m/e* 1130, and electron-impact mass spectra produce weak signals around *m/e* 900. Structure **4** contains three NH protons with quite different environments. ^1H NMR spectrum indeed shows three signals at low field (δ 11.73, 9.98, and 8.70). Two of them disappeared in the presence of D_2O, and the third (8.70 ppm) could only be erased with D_2O in the presence of triethylamine. The NMR data also indicate that no other new carbon–carbon bond has been formed in the dimer: neither do any signals for tertiary or quaternary pyrrolin carbon atoms appear[6] nor are proton signals for substituted ethyl groups observed. Clues on the rigid conformational structure of dimer **4** can be deduced from the upfield region of the ^1H NMR spectrum. Two alkyl group signals are shifted upfield by about 0.6 ppm (δ_{CH_3} 0.58, δ_{CH_2} 2.02). This may be due to a ring current effect of one pyrrole ring on one ethyl group of the neighboring molecule. We assign these signals to ethyl groups on C-12^1 and C-12^2. Two other ethyl groups are shifted downfield (δ_{CH_3} 1.33, δ_{CH_2} 3.14). This may be rationalized if one assigns these signals to the ethyl groups on C-7^1 and C-7^2 and assumes an anisotropic shift of one ethyl group by

---

(7) Sheldrick, W. S., TU Braunschweig, personal communication. Luger, P.; FU Berlin, personal communication.

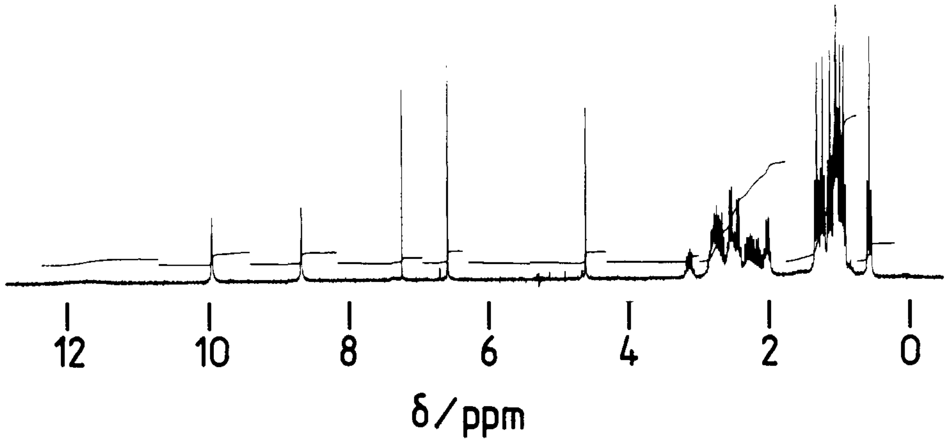


Figure 1. ^1H NMR spectrum (in $CDCl_3$) of dimer **4** and its proposed conformation (δ = observed chemical shift; Δ = $Eu(fod)_3$-induced relative shifts, see Experimental Section).

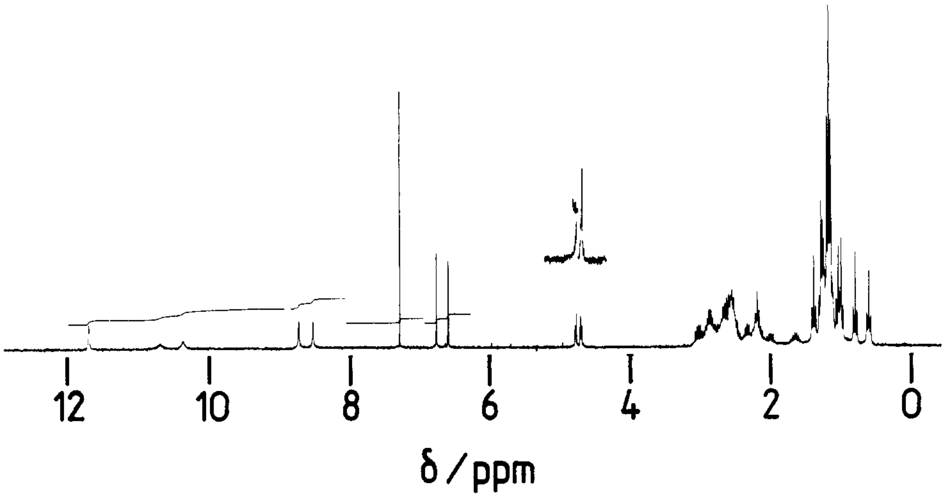


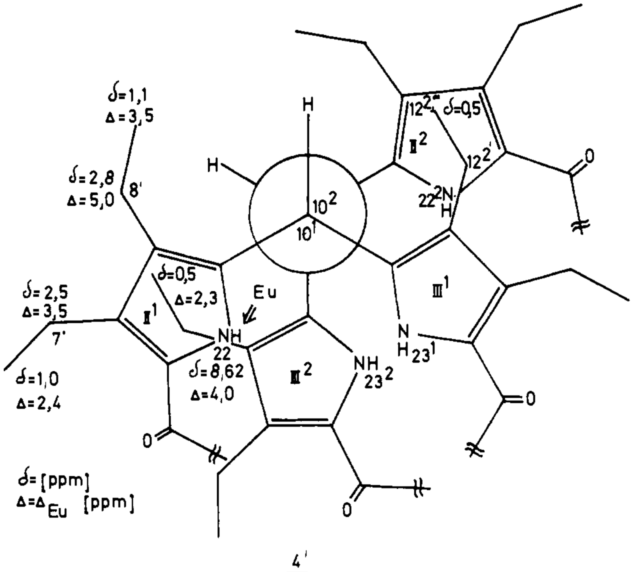
Figure 2. ^1H NMR spectrum (in $CDCl_3$) of dimer **5**.

one carbonyl group. Both groupings could be forced into a single plane by steric repulsion within the dimer molecule. The situation is made clear by the Newman projection of the gauche conformation of carbon atoms 10^1 and 10^2 (structure **4′**). Dreiding models show that this is the least hindered conformation, since in the anti conformation two more ethyl groups would strongly interact with two pyrrole rings of the neighbor molecule.

The methylene group signal at δ 3.14 is a multiplet which collapses to a doublet on irradiation at δ 1.33. The reverse experiment reduces the triplet at δ 1.33 into a doublet. Therefore, following the assignments deduced above, methylene protons at C-7^1 and C-7^2 are diastereotopic. The same is true for the CH_2 multiplet at δ 2.30. It produces a doublet on double irradiation at δ 1.16. We assign it to the ethyl groups on C-13^1 and C-13^2. All other ethyl groups collapse to singlets on irradiation at the appropriate frequencies.

Experiments with $Eu(fod)_3$ were analyzed by the relative method of Roth and Rewicki.[8] Relative shifts of proton signals are in the following order: NH-(22) (δ 8.7) > CH_2-(8′) (δ 2.78) > CH_2-(7′) (δ 2.4) > CH-(10) (δ 4.64) > CH_3-(12′) (δ 0.53). The shift reagent coordinates to the same nitrogen atom which is deprotonated most slowly (see above). This should be N-22 which is protected by the ethyl group against the attack of bases. It is also more basic than the other nitrogen atoms, because the in-plane keto group reduces the aromaticity of the pyrrole ring. This conclusion is supported by the up-field shift of the NH signal as compared with those of the other pyrrolic NH signals. The substituents of pyrrole ring II therefore undergo the largest contact shifts, and the signal at δ 2.78, 2.4, and 1.0 can be assigned.

The only methyl group (δ 0.53) which undergoes a large shift is the one that is fixed over the pyrrole ring which coordinates to the shift reagent. The linearity of all relative shifts indicate the homogeneity of the sample, and the observed order is in complete agreement with predictions based on structure **4** in the gauche conformation **4′** given in Figure 1.



4′

Unsymmetrical Dimer of Dioxoporphodimethene. Compound B (mp 271–273 °C) from the TLC exhibits properties (elemental

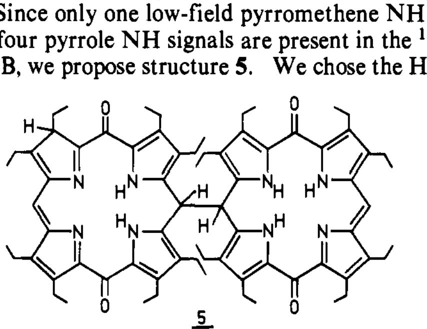
---

(8) Roth, K.; Rewicki, D. *Kontakte* **1978**, *2*, 9.

analysis, electronic, infrared, and electron-impact and field desorption mass spectra) similar to those of compound A, now identified as dimer **4**. Both compounds, dimer **4** and B, were stable for several hours in chloroform solution. After extended storage, however, pure **4** partly converted to B and vice versa. The interconversion was accelerated by acids, and after longer reaction times dioxoporphodimethene **2b** was also produced. Compound B may therefore be a tautomer of dimer **4**.

The ^{1}H NMR spectrum of B contains two signals for methine protons at an unsaturated methine bridge (δ 6.58 and 6.98) and two doublets for methine protons at δ 4.76 and 4.70 (J_{AB} = 5 Hz). Since two of the carbon bridges are carbonyl groups, this pattern gives the most straight forward proof of a dimer. Only in a dimer of a dioxoporphodimethene can four methine protons occur and only in a dimer can one methine proton per macrocycle produce an AB signal. The latter signal also proves the existence of a covalent bond between both monomers.

What is the origin of the unsymmetry in compound B? A partial answer comes from the experiments cited above. Since the elemental analysis points to a dioxoporphodimethene, we can exclude any salt formation or reversible addition reactions of nucleophiles, e.g., hydrate formation. The reversible, acid-catalyzed formation of dimer A from B renders a tautomerization rather probable. This is substantiated by the ^{1}H NMR spectrum which contains five signals of NH protons at δ 11.70, 10.69, 10.37, 8.72, and 8.52. This corresponds to the data for dimer **4** except that two signals are split. Only one dipyrromethene NH at low field is present. This indicates that one of the six NH protons has migrated to another atom. Obvious candidates as proton acceptors would be the carbonyl oxygen atoms. The ^{13}C NMR spectrum, however, contains four signals for carbonyl carbons. There is again no signal for an enol carbon atom, and the infrared spectrum clearly shows the absence of OH groups. Since we have already been accounted for the carbon bridge atoms (four C=O and four CH), only the α- and β-pyrrolic carbon atoms remain as possible protonation sites. α-Pyrrolic carbon atoms can again be dismissed because the two signals for the 10^1- and 10^2-carbons are the only ^{13}C absorptions in the range between 20 and 117 ppm. An sp^3-hybridized carbon atom bound to a nitrogen atom, however, should absorb within this region. The remaining alternative is protonation of a β-pyrrolic site. Unfortunately, the regions of saturated hydrocarbons in ^{1}H and ^{13}C NMR spectra are overcrowded with signals and a β-pyrrolic methine proton or tertiary carbon atom could not be clearly identified. However, there is strong corroborative evidence for the assumption that one β-pyrrolic site has been protonated: two additional multiplets in comparison with those for **4** for one methylene group each appear at δ 2.09 and 1.62. These multiplets collapse to doublets if the methyl group signal at δ 0.78 is irradiated. These data provide strong support for the presence of one β-pyrrolic proton, although its absorption is hidden under strong methyl or methylene proton signals and could not be detected or indirectly located by double-irradiation experiments. An H-8 tautomer is excluded by a gated decoupled ^{13}C NMR spectrum, which does not display $^3J_{CH}$ couplings. Since only one low-field pyrromethene NH signal is present but four pyrrole NH signals are present in the ^{1}H NMR spectrum of B, we propose structure **5**. We chose the H-3 rather than the H-2 tautomer, because the large shift difference of the diastereotopic methylene protons (δ 2.09 and 1.62) could be explained by the anisotropy produced by a neighboring keto group.



5

5-Oxo-15-hydroxyporphodimethene. The most polar product, C, of the thallium oxidation of zinc octaethylporphyrin (**1b**) was easy to identify as **6** by spectroscopic analysis. One signal at δ 11.0 and one signal for two unsaturated methine protons signified two pyrromethene units. An additional signal at δ 5.38 was assigned to the methine proton of a secondary alcohol. A singlet at δ 175.57 and two doublets at δ 121.20 and 53.25 in the off-resonance decoupled ^{13}C NMR spectrum also indicated the presence of three protonated methine bridges and one carbonyl bridge. The symmetry of the spectra is only compatible with that of structure **6**. Formation of a zinc complex is accompanied by dehydrogenation to yield **2a**. Mass spectra of **6** do not show any sign of dimers.

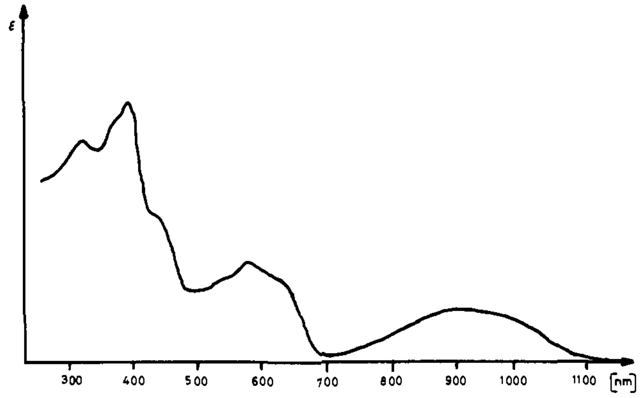
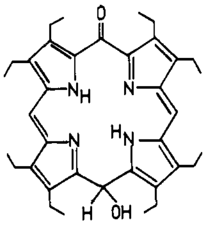


Figure 3. Electronic spectrum of the olefinic dimer **7b** (in CHCl$_3$).

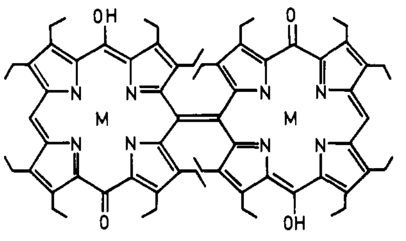


6

Olefinic Dimer. Complexation of dimers **4** and **5** with zinc acetate was very slow. Several hours of refluxing in dichloromethane in the presence of oxygen produced a grayish green compound, being more polar on TLC (CHCl$_3$, R_f 0.2) than the starting materials but not as polar as a charged porphyrin derivative. This product gave an elemental analysis for a zinc complex of a dioxoporphodimethene and a field desorption mass spectrum corresponding to that of a dimer containing two zinc ions. The dimer peak was stronger than that in the spectra of dimers **4** and **5**. The electronic spectrum contained a strong absorption near 900 nm.

In the infrared spectrum the three NH absorptions at 3430, 3400, and 3360 cm^{-1} of dimers **4** and **5** are replaced by one broad band at 3360 cm^{-1}. The ^{1}H NMR spectrum showed only one methine proton signal at δ 6.03 and several multiplets for the ethyl protons. The ^{13}C NMR spectrum exhibited only one carbonyl carbon singlet at δ 183.48 and a singlet at δ 164.21 which we assigned to a phenolic carbon atom. The data indicate that the metalation has been accompanied by a proton shift from nitrogen to oxygen and dehydrogenation of the linked carbon bridge atoms. Structure **7b** summarizes these results.

Dimer **4** could also be dehydrogenated with dichlorodicyanobenzquinone (DDQ). A green compound with a broad absorption band centered at 710 nm and a shoulder at 760 nm was isolated in 83% yield. The field desorption mass spectrum indicated that this compound could still be a dimer. The ^{1}H NMR contained only one signal at δ 6.57 for a proton at an unsaturated methine bridge. Three signals at δ 13.86, 14.07, and 14.5 are assigned to two pyrrole NH protons and one enolic OH proton. The enol tautomer **7a** is chosen because it could explain the long wavelength absorptions observed in the visible range of the spectrum and because of its analogy to zinc complex **7b**. Metalation of **7a** with zinc acetate leads to **7b** in quantitative yield. Treatment of dimer



7a, M = 2H
b, M = Zn
c, M = Cu

5 with DDQ produces the identical zinc complex **7b** under the same reaction conditions.

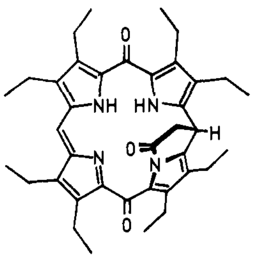
Demetalation of **7b** with concentrated hydrochloric acid led to a mixture of the hydrogenated dimers **4** and **5** (≤50%) together with several unidentified products. The reason and the mechanism of these reduction or disproportionation reactions are not understood and caused considerable confusion at the beginning of this investigation.

The evidence for the olefinic dimer structure **7** may be summarized as follows. (a) **7** is formed by the action of dehydrogenating and oxidizing agents from dimers **4** and **5**. (b) Acid treatment of **7b** leads to dimers **4** and **5** in a combined yield of approx. 50%. (c) A charged structure for metal complex **7b** can be excluded from elemental analysis and TLC behavior. (d) ^{1}H NMR spectra show a complex pattern for four ethyl groups but only one methine proton at δ 6.1 (**7b**) or 6.6 (**7a**). (e) Field desorption mass spectra are consistent with that for a stable dimer. (f) The same is true for the absorption band in the near-infrared spectra. Structure **7** is tightly linked with structure **4**. Since this structure is unequivocally proven, we think that the same holds true for **7**.

We also synthesized the corresponding copper complex **7c** which gave similar elemental analysis and electronic and infrared spectra. The esr spectrum of **7c** consists of the usual four-line copper pattern with hyperfine splitting (nine lines) in the high-field part.[12] No line broadening as a sign of copper–copper interactions in the dimer could be detected at room temperature.

7a and **7b** are two of the most highly substituted olefins reported so far in the literature. They constitute extreme cases of "sterical overcrowding of the porphyrin plane"[11] as well. They are probably only stable because the macrocycles of **7a,b** are highly flexible and because the substituents of the "olefinic" double bond can distribute its p electrons to form dipolar resonance structures.

Acetylations. Since Smith[2] and Dörffel[9] have used acetyl derivatives to characterize dioxoporphodimethenes, we also acetylated dimer **4** with acetic anhydride in pyridine. A good yield of a monoacetylated derivative was formed, but its spectroscopic data indicated that the expected O-acetylation had not taken place. Since nitrogen and carbon acetylation can lead to several products, we first repeated the acetylation of dioxoporphodimethene **2b** described by Dörffel.[9] He had favored, on the basis of ^{1}H NMR and infrared data, a cyclobutanone derivative in which the carbonyl group of the dehydrated acetic acid was attached to a methine bridge carbon atom and the methylene group to an α-pyrrolic carbon atom. This structure can now be dismissed on the basis of better resolved ^{1}H NMR and ^{13}C NMR spectra. The latter shows two absorptions for carbonyl carbons at δ 168.6 and 168.0, which point to an acid derivative rather than to a ketone. Clear-cut evidence that the acetylation product of **2b** is a mixture of diastereomeric lactams **8** may be derived from two doublets at δ 123.6 and 1229 for unsaturated methine bridge carbons, a triplet at δ 42.3 for a methylene group adjacent to a carbonyl carbon, and a doublet at δ 29.0 for a saturated methine carbon atom in the off-resonance decoupled ^{13}C NMR spectrum. These structures are also proven by the ^{1}H NMR spectra. One methine proton singlet at δ 6.93 for CH-(20), a doublet for CH-(10) at δ 4.51, two doublets at δ 3.52 and 3.57 for H$_A$, and two singlets at δ 3.22 and 3.29 for H$_B$ as well as two NH proton signals at δ 10.2 and 11.68 are observed. The lack of intense fragment ion peaks in the mass spectrum and the infrared spectrum ($\bar{\nu}$ = 1760 cm^{-1}) are also in accordance with those of the proposed structure **8**. Acetylations of dimers **4** and **7b** under the same conditions as applied to dioxoporphodimethene **2b** also produce **8**. Surprisingly, the mass spectra of **8** do sometimes provide evidence for a dimer. If **8** is isolated from pure chloroform, one obtains a field desorption mass spectrum with the strongest peak at m/e 1214. In the presence of hydrochloric acid however, this dimer is destroyed. The units of the lactam dimer are therefore certainly not connected by covalent bonds. We propose a hydrogen bridge between the pyrrolic NH and the carbonyl group of the lactam. This interpretation is supported by the observation that the ^{1}H NMR signal at δ 10.1 for the pyrrole proton involved is exceptionally broadened. Similar hydrogen-bridged dimers have been described with several other α-carbonyl-substituted pyrrole derivatives.[10] Dimers **4**, **5**, and **7** on the other hand do not dissociate in polar solvents.

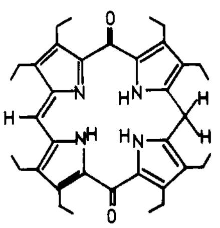


8

In another acetylation procedure of (5,15-dioxoporphodimethene)zinc complex **2b** we used acetic anhydride and catalytic amounts of sulfuric acid. The porphyrin diacetate **1e** was obtained in only 6% yield. The phyllo-type UV/visible spectrum is similar to the one described by Smith[2] for the assumed 5,10-diacetate. The ^{1}H NMR spectrum reveals two singlets each for the methine bridge and the methyl protons of the acetyl groups. The splitting of these signals is certainly due to two compounds (syn and anti diacetates?), which we have not been able to separate.

Redox Chemistry of Dimers 4 and 5. The dehydrogenation of dimers **4** and **5** to **7a** does not occur on a platinum electrode. Up to 1.5 V no oxidation step is found in the cyclic voltammogram of approximately 10^{-4} M dichloromethane solutions of either both dimers or dioxoporphodimethenes **2a,b**.

Chemical reduction of dioxoporphodimethenes **2a,b** with sodium borohydride leads to hydrogenation of one methine bridge and one nitrogen atom. The product **9** can be isolated and has been described earlier as a reduction product of *meso*-tetraoxoporphinogens.[13] Treatment of **2b** with lithium aluminum hydride in the presence of air produces octaethylporphyrin as the only isolable product. Dimers **4** and **7** are converted by the same hydrides to identical monomeric products. Cyclic voltammetry of dioxoporphodimethenes **2a,b** and dimers **4**, **5**, and **7** in Me$_2$SO all show two two-electron reduction steps around −0.3 and −1.0 V vs. SCE (see Experimental Section).



9

---

[9] Dörffel, J. Dissertation, Braunschweig, 1969.

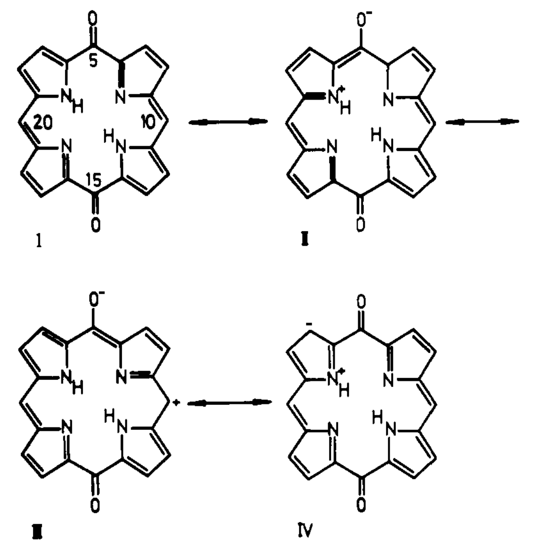
[10] Gossauer, A. "Die Chemie der Pyrrole"; Springer: Berlin, 1974; p 70.

[11] Woodward, R. B. *Ind. Chim. Belge* **1962**, 1293.

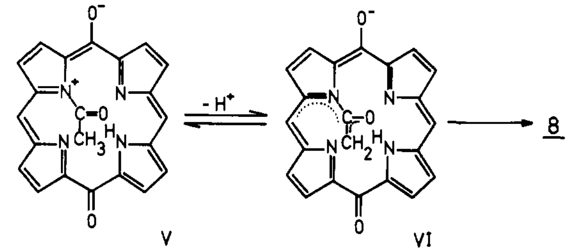
[12] Subramanian, J. In Smith, K., Eds.; "Porphyrins and Metalloporphyrins"; Elsevier, New York, **1975**; pp 562 ff.

[13] Inhoffen, H. H.; Fuhrhop, J.-H.; v. d. Haar, F. *Liebigs Ann. Chem.* **1966**, *700*, 92.

Scheme I



Scheme II



Discussion

Our results can be rationalized if one considers 5,15-dioxoporphodimethenes as reductone analogues in which the interactions between neighboring oxygen and nitrogen atoms are most important. The low frequencies of the C=O infrared ($\bar{\nu}$ = 1600 cm^{-1}) and the low-field ^1H NMR NH absorption (δ 11–14), the lower stability of metal complexes as compared to that of porphyrins, and the nonelectrophilicity of the carbonyl group (hydride, alcohols, and water are not added) point to charge distribution as in II. The fact that oxidation of porphyrins generally stops at the 5,15-dioxo stage and that trioxo- and tetraoxo derivatives can only be obtained under conditions of force also indicate that the methine bridges 10 and 20 are relatively electropositive as those are in III. The hydride addition to this position and the low-field absorption of CH-(15,20) in the ^1H NMR spectrum support this view. Another charge separation, IV, may also occur. It gives an example of a polar structure in which the pyrrole electron sextet is retained and it would explain the tautomerization of **4** to **5**.

The formation of dimer **4** and the acetylation of **2a** leading to **8** remain to be explained. Several oxidative couplings of benzene derivatives with the aid of thallium(III) salts have been reported.[14] In our case two molecules of dioxoporphodimethene are coupled without dehydrogenation of the coupling site. An analogous oxidation of 9-methoxyanthracene to bianthron-9-yl has been described recently.[14] We assume that the zinc 5,15-bis(trifluoroacetoxy)porphyrin complex **1h** is oxidized by thallium(III) to the π-cation radical and this dimerizes spontaneously. This anomalous reaction is favored by the ruffled conformation of the disubstituted porphyrin ligand and by a localization of unpaired spin density on the methine bridges. If the carbonyl groups are removed, e.g., by hydride reduction, the dimer dissociates. Dehydrogenation to form a highly hindered, twisted tetra-substituted ethene derivative is on the other hand possible.

Acetylation of **2b** in pyridine may occur by substitution of the acid proton in II by an acylium ion. The positive charge in the N-acetylated intermediate V together with proton-attracting forces of the other nitrogen atoms could then promote deprotonation of the methyl group which is followed by irreversible cyclization to **8**. Since the acetylation occurs only under conditions of force, we assume that the dimers are decomposed to monomeric **8b** before acetylation occurs.

Table I. Eu(fod)$_3$ Shift Experiments (Relative Method)[8]

$\delta°$	$\delta_0{}^b$				
	I	II	III	IV	V
4.58^a	4.71	6.03	6.08	6.30	6.92
0.52	0.65	1.88	1.94	2.17	2.76
0.89	0.85	0.56	0.54	0.48	0.34
0.99	1.09	1.86	1.90	2.05	2.38
1.10	1.28	3.30	3.38	3.65	4.62
1.98	2.10	3.14	3.20	3.38	4.82
2.39	2.50	3.55	3.60	3.77	4.23
2.50	2.75	4.70	4.84	5.10	6.05
2.75	3.00	5.83	5.91	6.40	7.75
6.55	6.57	6.87	6.88	6.93	7.05
8.62	8.88	11.09	11.18	11.55	12.09
9.92	10.00	10.89	10.93	11.09	11.55

[a] The signal at δ 4.58 was taken as a reference. [b] The shifts δ_0 reported in columns I–V, corresponding to rising amounts of Eu(fod)$_3$, are differences of the signal indicated minus the shift of the reference signal. The signals given were shifted most strongly by Eu(fod)$_3$; lesser shifts are omitted.

Experimental Section

Melting points were measured on a Kofler microscopic hot-stage apparatus. TLC monitoring of all reactions was performed by using Merck silica gel 60 F-254 precoated sheets (0.2 mm), and preparative TLC was carried out on 20 × 100 cm glass plates coated with Woelm DC 04671 silica gel (1 mm) without gypsum or indicator. Electronic spectra were determined by using a Cary 17 spectrometer, ^1H NMR and ^{13}C NMR spectra were measured with tetramethylsilane as internal standard at 270 MHz (Bruker WH 270). Mass spectra were either measured at a CH 5 DF or field desorption MAT 311 A spectrometer.

Zinc octaethylporphyrin was prepared according to standard literature procedures.[15] Tetrahydrofuran was refluxed over lithium aluminum hydride and distilled, as were all other solvents used.

Thallium(III) Oxidation of Zinc Octaethylporphyrin 1a. A 1.5-g sample of **1a** in 1.5 L of dry CH_2Cl_2 and 250 mL of dry THF was treated with 1.68 g of TTFA, and the solution was stirred for 15 min. A color change from red to violet was observed. Then 1.52 g of TTFA in 250 mL of THF was added, and the mixture was stirred for another 15 min. SO_2 was then bubbled in a rapid stream through the solution for 30 s, and 20 mL of concentrated HCl in 100 mL of THF was added. After 5 min of stirring the white precipitate of TlCl was filtered off and washed with CH_2Cl_2. The combined organic phases were washed three times with 0.5 L of water, dried (Na_2SO_4), and evaporated to dryness. This procedure is identical with the one described by Smith,[2] except for the scale of preparation.

The product mixture was chromatographed on 25 1-m preparative TLC plates with $CHCl_3$ as eluant, and five products were isolated after crystallization from chloroform–methanol: 5,15-dioxoporphodimethene **2b** (R_f 0.9, 130 mg, 9% yield), dimer **4** (R_f 0.6, 270 mg, 19%), dimer **5** (R_f = 0.5, 200 mg, 14%), oxyporphyrin **1d** (R_f 0.2, 240 mg, 17%), 5-oxo-15-hydroxyporphodimethene **6** (R_f 0.0, rechromatographed with $CHCl_3$–CH_3OH, 9:1, R_f 0.3, 150 mg, 12%). Total yield of crystallized oxidation products was 71%.

5-Hydroxyoctaethylporphyrin 1d. It occurred as the oxophlorin tautomer and was identical with an authentic probe on TLC and in electronic and infrared spectra.

5,15-Dioxooctaethylporphodimethene 2b. This product was identical with an authentic probe on TLC and in electronic, infrared, and ^1H NMR spectra in $CDCl_3$: ^1H NMR (in CF_3COOD) δ 7.98 (2 H, s, 2 meso-H), 2.7–3.0 (16 H, m, 8 CH_2), 1.1–1.5 (24 H, m, 8 CH_3); ^{13}C NMR (in $CDCl_3$) δ 174.44 (C=O), 137.60, 129.68, 126.24, 121.56 (pyrrole C), 123.28 (methine C), 17.98, 16.41, 15.80, 14.22 (ethyl C); ^{13}C NMR (in $CDCl_3$, off-resonance decoupled) δ 123.28 (d), 17.98, 16.41 (t, CH_2), 15.80, 14.22 (q, CH_3).

10^1,10^2-Bis(5,15-dioxo-10^1,10^2-dihydrooctaethylporphodimethene) (4): mp 289–291 °C; Electronic spectrum λ_{max} 537 nm (ϵ 15800), 344 (56000), 293 (52000); IR (KBr) 1605 cm^{-1} (s, C=O) 3465, 3450, 3430

---

(14) McKillop, A.; Turrell, A. G.; Youngart, E. W.; Taylor, E. C. *J. Am. Chem. Soc.* **1980**, *102*, 6504.

(15) Fuhrhop, J.-H.; Smith, K. M. "Laboratory Methods in Porphyrin and Metalloporphyrin Chemistry"; Elsevier, New York, 1975.

Table II. Double-Irradiation Experimental Data for Compound 4

		multiplicity of signals	
ν_2	δ	normal	with DI
3.14	1.33	t	d
2.79	1.10	t	s
2.30	1.16	t	d
2.02	0.58	t	s
0.58	2.02	m	s
1.10	2.79	m	m[a]
1.16	2.30	m	m
1.33	3.1	m	d

[a] Less complicated.

Table III. Double-Irradiation Experimental Data for Compound 5

		multiplicity of signals	
ν_2	δ	normal	under DI
4.76	4.70	d	s
1.62	0.78	t	d
2.12	0.58	t	s
0.78	1.62	m	d
1.35	3.02	m	m[a]

[a] Less complicated.

cm^{-1} (m, NH); Mass spectrum (electron impact, 200 °C, 70 eV), *m/e* 566 (0.5 M^+, 100%), 564 (30%), 537 (25%), 283 (25%); mass spectrum (330 °C, 4 eV), *m/e* 1128 (≤1%), several peaks (≤1%) in the range between *m/e* 590 and 1200, 592 (20%), 584 (~70%), 566 (100%); mass spectrum (field desorption, FDI = 7.8 kV, U_B = 2 kV, slow heating of the filament which had been dipped into an acetone solution of **4**), several peaks in the range from *m/e* 1128 (100%) to 1133 (30%); ^1H NMR ($CDCl_3$), δ 11.73 (2 H, br s, exchangeable with D_2O, NH), 9.98 (2 H, s, exchangeable with D_2O), 8.70 (2 H, s, did exchange with D_2O only in the presence of triethylamine), 6.62 (2 H, s, olefinic CH), 4.64 (2 H, s, aliphatic CH), 3.14 (2 H, m, aliphatic CH), 1.9–2.9 (30 H, m, CH_2), 0.9–1.35 (42 H, 1 t, CH_3), 0.58 (6 H, t, CH_3) [polar solvents (Me_2SO, pyridine, H_2SO_4, all deuterated) did not have pronounced effects on the ^1H NMR spectra, the methine proton signals at δ 6.6 and 4.6 were always observed in a ratio of 1:1]; ^{13}C NMR ($CDCl_3$, ^1H noise decoupled) δ 176.88, 174.51 (C=O), 152.80, 151.02, 143.93, 142.45, 139.50, 137.22, 137.02, 136.44, 135.49, 133.55, 133.45, 131.41, 130.62, 128.60, 126.51, 126.04 (pyrrole CH), 120.56 (olefinic methin CH), 38.32 (aliphatic methin CH), 18.99, 18.46, 18.03, 17.78, 17.57, 17.52, 17.05, 16.99, 16.82, 16.77, 16.36, 15.23, 14.08 (ethyl); ^{13}C NMR ($CDCl_3$, off-resonance proton decoupled) δ 120.56 (d), 38.32 (d), 14.08 (q); ^{13}C NMR (gated decoupled) the singlet at δ 38.32 was split into two doublets ($^1J_{CH}$ = 128.5 Hz, $^2J_{CH}$ = 5.5 Hz).

Anal. Calcd for $C_{72}H_{90}N_8O_4$ (M_r = 1131.6): C, 76.42; H, 8.02; N, 9.90. Found: C, 76.40; H, 8.40; N, 7.91.

3-Hydro-21-dehydro-10^1,10^2-bis(5,15-dioxo-10^1,10^2-dihydrooctaethylporphodimethene) (5). This is compound B from the thallium oxidation described at the beginning of the Experimental Section: mp 271–273 °C; Electronic spectrum λ_{max} 511 nm (ϵ 17 000), 400 (25 500), 332 (sh, 50 300), 314 (sh, 50 600), 297 (57 500); IR (KBr) 1605 (s, C=O); mass spectrum (electron impact, 70 eV, 300 °C), *m/e* 566 (100%); mass spectrum (field desorption, U_B = 2 kV, FDI = 5.6 kV), *m/e* 1131 (100%); ^1H NMR ($CDCl_3$) δ 11.70 (1 H, s, exchangeable with D_2O, NH), 10.69, 10.37 (2 H, br, exchangeable with D_2O, NH), 8.72, 8.52 (2 H, s, exchangeable with D_2O only in the presence of triethylamine), 6.98, 6.59 (2 H, s, methin), 4.76, 4.70 (2 H, dd, J_{AB} = 5 Hz), 1.89–3.09 (30 H, m, CH_2CH_3), 1.62 (2 H, m, CH_2CH_3), 1.35 (3 H, m, CH_2CH_3), 0.9–1.3 (39 H, m, CH_2CH_3), 0.78 (3 H, t, CH_2CH_3), 0.58 (3 H, t, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 175.76, 175.02, 173.85, 172.68 (C=O), 147.68, 146.29, 144.59, 141.39, 139.17, 138.07, 137.92, 137.33, 137.26, 136.98, 136.65 (2 C), 136.54, 136.45, 136.06, 135.59, 135.20 (2 C), 135.14, 133.32, 132.94 (2 C), 132.72, 132.03, 131.30, 128.92, 127.78, 127.45, 127.34, 126.63, 125.46, 124.50 (pyrrolic), 120.58, 117.62, 39.50, 38.35 (methine), 18.90, 18.84, 18.60, 18.39, 18.25, 18.02, 17.68, 17.63, 17.49, 17.35, 17.06, 17.01, 16.76, 16.58, 16.20, 16.14, 15.40, 15.31, 15.25, 15.17, 15.03, 14.16 (ethyl); ^{13}C NMR (off-resonance decoupled) doublets at δ 120.58, 117.62, 39.50, 38.35; ^{13}C NMR (gated decoupled) singlets at δ 39.50, 38.35 split into doublets ($^1J_{CH}$ = 128.5 Hz, $^2J_{CH}$ = 5.5 Hz).

Tautomerization of Dimers 4 ⇌ 5 and Conversions to Monomer 2b. A 10-mg sample of dimer **4** was dissolved in 50 mL of chloroform–methanol (1:1), and the solution was left standing at room temperature for 14 days. HPLC on DIOL (Merck, 5 µm, 12.5-cm column) gave 14.9% of 5,15-dioxoporphodimethene **2b**, 74.5% of dimer **4**, 5.8% of dimer **5**, and 4.8% of unidentified products.

The same procedure was applied to 5 mg of dimer **5** and 2.8% of **2b**, 43.4% of dimer **4**, 47.9% of dimer **5**, and 5.9% of unidentified products were found. Dimers **4** and **5** and monomer **2b** were characterized by TLC and IR, mass, and electronic spectra. **2b** was also converted into its zinc complex. In several cases it was observed that dimers **4** and **5** decomposed almost quantitatively on extended standing in solution, and **2b** was then the only isolable product in up to 40% yield.

These experiments indicate that dimer **4** is relatively much more stable than dimer **5**. This was verified during several experiments, in which pure dimer **5** became contaminated with **4**, particularly in the presence of acids. Dimer **4** was much less bothersome.

Reduction of Dimers 4 and 5 to Octaethylporphyrin 1c. A 5-mg sample of dimer **4** or of dimer **5** in 10 mL of dry THF was treated with approximately 50 mg of lithium aluminum hydride and the solution was stirred for 5 min. A 3-mL sample of ethyl acetate and 3 mL of water were added. The solution was extracted with chloroform, washed, and dried (Na_2SO_4). Octaethylporphyrin was isolated by preparative TLC ($CHCl_3$) and identical with an authentic probe on TLC and in IR, mass, and electronic spectra.

5-Oxo-15-hydro-15-hydroxyoctaethylporphodimethene (6). This is product C of the thallium oxidation of zinc octaethylporphyrin: mp 267–270 °C; Electronic spectrum λ_{max} 543 nm (5900), 413 (9500), 310 (22 800); IR 1605 (s, C=O), 3360 cm^{-1} (m, OH); mass spectrum, *m/e* 566 (M^+, 15%), 564 ($M^+ - 2$, 100%), 549 (15%), 535 (28%), 506 (9%); ^1H NMR (in $CDCl_3$) δ 11.0 (2 H, s, exchangeable with D_2O, NH), 6.88 (2 H, s, methine), 5.38 (1 H, s, $C\mathit{H}OH$), 2.0–2.8 (16 H, m, $C\mathit{H}_2CH_3$), 0.8–1.3 (24 H, m, $CH_2C\mathit{H}_3$); ^{13}C NMR δ 175.57 (C=O), 143.37, 137.48, 135.67, 129.51, 127.72, 126.49 (pyrrole), 121.20 (methine), 53.25 ($C\mathit{H}OH$), 18.58, 18.29, 17.43, 16.88, 16.61, 15.97, 15.39, 15.09 (ethyl); ^{13}C NMR (off-resonance decoupled) doublets at δ 121.20 and 52.25.

Anal. Calcd for $C_{36}H_{46}N_4O_2$ (M_r = 566.8): C, 76.56; H, 7.85; N, 9.92. Found: C, 76.23; H, 8.09; N, 9.48.

A 5-mg sample of 6 was refluxed for 10 min in a mixture of 20 mL of dichloromethane and 1 mL of methanol saturated with zinc acetate. A color change from brown to red was observed. Preparative TLC and recrystallization from chloroform–methanol yielded zinc 5,15-dioxoporphodimethene (**2a**) as the only product.

10^1,10^2-Bis(5,15-dioxo-10^1,10^2-dehydrooctaethylporphodimethene) 7a, Its Zinc Complex 7b, and Its Copper Complex 7c. (A) 7a from Dimer 4 by Dehydrogenation. A 30-mg sample of dimer **4** in 20 mL of dry THF was treated with 50 mg of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DCCB) at 75 °C. A color change from red to green was observed. After 30 min all starting material had disappeared as was shown by TLC monitoring. Removal of solvent preparative TLC ($CHCl_3$) and crystallization from chloroform–methanol yielded 25 mg (83%) of **7a**: electronic spectrum λ_{max} 765 nm (ϵ 3900), 710 (5000), 450 (s, 12 000), 410 (s, 20 900), 368 (52 400), 352 (44 100), 320 (22 100); IR 1585, 1605 cm^{-1} (C=O), 3360 cm^{-1} (sharp, OH); ^1H NMR ($CDCl_3$) δ 14.50 (br s, OH), 13.86 (4 H, s, exchangeable with D_2O, NH_3), 6.57 (2 H, s, methine), 2.78, 2.66 (8 H, q, CH_2CH_3), 2.51 (16 H, m, CH_2CH_3), 1.0–1.22 (48 H, m, CH_2CH_3).

(B) 7b by Metalation of 7a. A 5-mg sample of the above dehydrogenation product was refluxed with 5 mL of dichloromethane and 1 mL of saturated zinc acetate solution in methanol for 10 min. After washing with water, removal of solvent, and preparative TLC, 2 mg of **7b** was isolated. Its qualitative electronic spectrum and its behavior on TLC were identical with the corresponding properties of **7b** described under C below.

(C) 7b by Metalation of Dimer 4. A 100 mg sample of dimer **4** in 150 mL of dichloromethane and 5 mL of saturated zinc acetate in methanol were refluxed for 15 h. Workup and chromatography as described under B and crystallization from chloroform–methanol yielded 98 mg (88%) of **7b**: mp >350 °C; electronic spectrum ($CHCl_3$) λ_{max} 1205 nm (ϵ 450), 985 (sh, 4570), 901 (5390), 635 (sh, 7400), 578 (9300), 538 (sh, 7600), 437 (sh, 13 300), 388 (45 200), 366 (sh, 36 700), 315 (26 600); IR 1580 cm^{-1}; mass spectrum (electron impact, 70 eV, 300 °C), *m/e* 622 (100%) 609 (100%); (electron impact, 2.9 ν, 400 °C) 1252 (2%); mass spectrum (field desorption U_B = 2 kV, FDI = 4.6 kV), 1257 ($M^+ + 1$, 100%); ^1H NMR ($CDCl_3$) δ 6.03 (2 H, s, methin), 2.60, 2.33 (32 H, m, CH_2CH_3), 1.00 (48 H, 6, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 183.48 (C=O), 164.21 (COH), 150.39, 148.00, 147.15, 143.80, 140.86, 138.99, 137.75 (pyrrole), 125.97 (methin), 18.39, 17.16, 16.58, 15.90, 15.26 (ethyl).

Anal. Calcd for $C_{72}H_{84}N_8O_4Zn_2$ (M_r = 1256.3): C, 68.84; H, 6.74; N, 8.92. Found: C, 68.65; H, 7.40; N, 6.06.

Table IV. Double-Irradiation Experimental Data for Compound 8

ν_2	δ	multiplicity of signals	
		normal	with DI
4.48	3.53	d[a]	s[b]
	3.43	d	s
	3.24	d	s
	3.14	d	s

[a] ABX system. [b] AB System.

(D) 7b by Metalation of Dimer 5. A 50-mg sample of dimer **5** was treated in the same way as dimer **4** described above. Yield: 45 mg (85%) of **7b** TLC, IR, and electronic spectra were identical with the data given above.

(E) 7c by Metalation of Dimer 4. A 50-mg sample of **4** was refluxed for 5 h with 100 mL of dichloromethane and 3 mL of a saturated solution of copper sulfate in methanol. Workup, chromatography, and crystallization as described above yielded 45 mg (80%) of copper complex **7c**: mp >350 °C; electronic spectrum λ_{max} 1203 (ϵ 760), 958 (3900), 662 (sh, 4800), 608, 547 (6600), 508 (6650), 391 (33 700), 375 (sh, 29 000), 317 (20 800); IR 1580 cm^{-1} (s, C═O); ESR ($CHCl_3$, room temperature) $\langle g_x \rangle$ 2.070, no line broadening as compared to copper octaethylporphyrin.

(F) 7c by Metalation of Dimer 5. A 5-mg sample of dimer **5** was refluxed in a mixture of 120 mL of dichloromethane and 1 mL of saturated copper sulfate in methanol. The copper complex obtained was identical (TLC, IR, electronic spectra) with the complex described under E.

5,15-Dioxo-10-hydro-10-(22-azacyclopentan-10′-on)octaethylporphodimethene (8). (A) From 5,15-Dioxoporphodimethene 2b. A 200-mg sample of **2b** was dissolved in 200 mL of pyridine and 60 mL of acetic anhydride and heated to 75 °C for 2 h. The solvent was removed and the residue purified by preparative TLC (silica gel, $CHCl_3$, R_f 0.3) and crystallization from CH_2Cl_2–MeOH: yield, 136 mg of red platelets (65%); mp 285–288 °C; electronic spectrum ($CHCl_3$)λ_{max} 546 nm (ϵ 19 300), 436 (sh, 19 600), 406 (22 300), 352 (24 500), 306 (43 100); IR (KBr) 1760 cm^{-1} (s, lactam) 1605 (s, C═O); mass spectrum (electron impact, 200 °C, 70 eV), *m/e* 608 (M^+ + 2, 12%), 606 (M^+, 100%), 591 (18%), 549 (8%); ^1H NMR ($CDCl_3$) δ 11.68 (s, 1 H, NH) 10.20 (br, 1 H, NH), 6.93 (s, 1 H ═CH), 4.51 (d, 1 H, CH), 3.54 (q, 1 H, CH), 3.27 (d, 1 H, CH), 2.44–3.02 (m, 14 H, CH_2), 2.30 (m, 2 H, CH_2), 1.0–1.3 (m, 21 H, CH_3), 0.93 (m, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 176.91, 175.17 (C═O-(5,15)), 168.64, 168.01 (C═O-(10″)) 148.48, 145.41, 144.11, 140.14, 138.77, 136.54, 134.34, 132.62, 129.43, 128.54, 121.78 (12 pyrrolic C), 123.66, 122.91 (═CH-(20)), 42.26 (CH_2-(10′)), 28.95 (CH-10)), 14.65–18.91 (13 signals for 16 ethyl carbons), off-resonance decoupled δ 123.66 (d), 122.91 (d), 42.26 (t), 28.95 (d).

Anal. Calcd for $C_{38}H_{46}N_4O_3$ (M_r = 606.8): C, 75.22; H, 7.64; N, 9.23. Found: C, 74.31; H, 7.59; N, 9.17.

(B) From Dimer 4. A 50-mg sample of dimer **4** in 100 mL of pyridine and 30 mL of acetic anhydride was heated for 1 h to 75 °C. The solvent was removed and the residue purified by preparative TLC ($CHCl_3$, R_f 0.25).

The product (38 mg, 70%) was isolated by evaporation of the solvent and by drying in vacuo: mp 301–304 °C; electronic spectrum λ_{max} 558 (s, ϵ 14 000), 511 (21 800), 355 (50 700), 305 (35 600); mass spectrum (electron impact) 606 (M^+, 100%); mass spectrum (field desorption), 1214 (2 M^+, 100%); ^1H NMR (CD_2Cl_2) δ 11.60 (1 H, s, NH, exchangeable with D_2O) 10.2 (1 H, br, NH exchangeable with D_2O), 6.84 (1 H, s, methine H), 4.48 (1 H, d, methine H), 3.53, 3.43 (1 H, 2 d, CH_2-(10′)), 3.24, 3.14 (1 H, 2 s, CH_2-(10′)), 2.3–2.8 (16 H, m, CH_2CH_3), 1.06–1.31 (21 H, m, CH_2CH_3), 0.89 (3 H, t, CH_2CH_3). The ABX system was also measured at higher resolution (10 Hz/cm). The signals at δ 4.48 (J_{BX} = 8 Hz, J_{AX} = 1.5 Hz) and δ 3.19 (J_{BX} = 18 Hz, J_{AX} = 1.5 Hz) were now split into quartets.

If the reaction products **8** from the acetylation of **2b** (procedure A) and **4** (procedure B) were dissolved in chloroform and the solution shaken with dilute hydrochloric acid, they showed identical electronic spectra and TLC behavior.

Table V.

compd	(1) reduction/ potential, V vs. SCE	(2) reduction/ potential, V vs. SCE	remarks
2a[a]	−0.57	−0.96	rev
4	−0.25	−0.80	
		−0.95	irrev
	−0.25	−0.76	
	−0.37	−1.00	irrev
7b	−0.33	−0.84	

[a] In CH_2Cl_2; 0.1 M in tetrabutylammonium perchlorate (TBAP), −0.50 and −0.80 V. Electrolysis in the ESR cuvette has been done with 0.5 mg of **2a** in CH_2Cl_2–TBAP. No ESR signal was observed.

(C) From Dimer 5. Acetylation and workup were carried in exactly the same way as described under B; yield 70%. Electronic, IR, mass (electronic impact), ^1H NMR, and ^{13}C NMR spectra are identical with the spectra described for B. TLC behavior was also the same.

(D) From Zinc Complex 7b: same findings as under C; 40% yield.

Zinc 5,15-Diacetoxyoctaethylporphyrin 1e and Free Base 1f. A 1.0 g sample of zinc dioxoporphodimethene **2b** in 300 mL of acetic anhydride and 0.5 mL of concentrated H_2SO_4 was heated for 1 h to 50 °C and poured into ice water. After neutralization and drying the solvent was removed and column chromatography ($CHCl_3$) was applied to the residue. Approximately 90% of starting material and 70 mg (6%) of **1e** were isolated and crystallized from chloroform–methanol: mp 321 °C; electronic spectrum ($CHCl_3$) λ_{max} 576 nm (ϵ 4700), 543 (15 400), 504 (2200), 414 (314 000), 335 (21 800); IR 1730, 1755 cm^{-1}, no band around 1600 cm^{-1}; mass spectrum *m/e* 712 (M^+, 70%), 669 (M^+ − CH_3CO, 20%), 653 (M^+ − CH_3COO, 42%), 626 (M^+ − $2CH_3CO$, 73%), 611 (M^+ − CH_3CO − CH_3COO, 100%), M^+ (calcd) 712.2967, M^+ (found) 712.2955; ^1H NMR ($CDCl_3$) δ 10.08 (2 H, s, methine-H), 3.9–4.2 (16 H, m, CH_2CH_3), 2.73 (6 H, s, $COCH_3$), 1.9 (24 H, m, CH_2CH_3).

Anal. Calcd for $C_{40}H_{48}N_4O_4Zn$ (M_r = 712.3): C, 67.27; H, 7.84; N, 6.77. Found: C, 66.76; H, 7.17; N, 7.01.

A 5-mg sample of **1e** was dissolved in 10 mL of chloroform and 2 mL of 0.1 N hydrochloric acid. A few crystals of sodium borohydride were also added. After neutralization and TLC ($CHCl_3$) 3 mg of **1f** was isolated: electronic spectrum ($CHCl_3$) λ_{max} 628 nm (ϵ 250), 576 (3200), 535 (2300), 504 (9800), 405 (113 000) (this spectrum is similar to the one reported by Smith[2] for 5,10-diacetoxyoctaethylporphyrin); IR 1725 and 1755 cm^{-1} (no band occurred around 1600 cm^{-1}).

Reduction of Zinc Dioxoporphodimethene (2a) to 5,15-Dioxo-10,10-dihydrooctaethylporphodimethene 9. A 20-mg sample of **2a** in 10 mL of chloroform was reduced with approximately 100 mg of sodium borohydride. After 30 min a few drops of 0.1 N HCl were added, until the solution turned green. If the addition of acid is omitted, no reduction is observed. The solution was then neutralized, dried (Na_2SO_4), and evaporated to dryness. Preparative TLC (R_f 0.37, $CHCl_3$) and crystallization from chloroform–methanol yielded 16 mg (80%) of **9**. Electronic, IR, ^1H NMR, and mass spectra were identical with those reported earlier for **9**.[13]

Cyclic Voltammetry of Dimers 4, 5, and 7b. The experimental procedure has been described earlier.[4] We used 0.1 M solutions of lithium perchlorate in freshly distilled Me_2SO. The concentrations obtainable with dimers **4**, **5**, and **7b** were approximately 2 × 10^{-4} M. The voltammograms were also run in solutions diluted to half with 0.1 M lithium perchlorate solution in Me_2SO. The peak heights of the reduction steps were then also cut in half. Potentials are summarized in Table V. All reduction steps corresponded to two-electron reductions. Electrolysis in the ESR cuvette has been done with 0.5 mg of **2a** in CH_2Cl_2–TBAP. No ESR signal was observed.

Acknowledgment. We thank Felicitas Lang for preliminary investigations and Professor Joern Müller, Technische Universität Berlin, for measurements of field desorption mass spectra. The Deutsch Forschungsgemeinschaft and the Fonds der Deutschen Chemischen Industrie supported his work.