

where the main products were reported to be acetic acid and methyl acetate, respectively.

Light emission is also observed when a Ce(IV) salt is added to a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and sodium pyruvate or when sodium pyruvate is added to a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ containing an excess of Ce^{4+} . In both cases, an orange light emission immediately appears. The same chemical experiment generates light emission with lactic and malonic acids and probably will occur with other organic acids or salts that can be rapidly oxidized by Ce^{4+} .

Note that one can produce ecl with the $\text{Ru}(\text{bpy})_3^{2+}$ -oxalate system in 1.0 M H_2SO_4 by adding Ce^{3+} to the solution. The light emission is weak in this case because of the low solubility of Ce(III)-oxalate. A strong emission occurs upon addition of Ce^{4+} to a mixture of oxalate and $\text{Ru}(\text{bpy})_3^{2+}$ in 1.0 M H_2SO_4 in the chemical experiment. An interesting point is that in the same system ($\text{Ru}(\text{bpy})_3^{2+}$, oxalate, 1.0 M H_2SO_4) addition of PbO_2 causes only a very low intensity light emission, which develops slowly, in spite of the fact that PbO_2 oxidizes both oxalate and $\text{Ru}(\text{bpy})_3^{2+}$ very rapidly. This difference in behavior between Ce(IV) and PbO_2 can be explained by the proposed mechanism. Ce^{4+} , which is a one-electron oxidant, reacts with oxalate to form the reactive intermediate very efficiently. On the other hand, on the solid PbO_2 the oxalate undergoes a direct two-electron oxidation which is ineffective for light emission. The low level light emitted by adding PbO_2 is probably only the result of the very

slow reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and oxalate in 1.0 M H_2SO_4 .

Conclusions

A new aqueous chemiluminescent and ecl system based on $\text{Ru}(\text{bpy})_3^{2+}$ and a suitable organic acid or salt (e.g., $\text{C}_2\text{O}_4^{2-}$) is described. The system produces quite bright emission and may be useful in practical ecl devices. The system is an example of a coupled chemical reaction¹⁵ with the observation of light emission as a probe of the reaction mechanism. The Ce^{3+} -oxalate system (or one with another organic acid or salt) provides a unique electrochemical system for carrying out a reduction under oxidizing conditions at the electrode surface (an "anodic or oxidative reduction"). Upon applying a sufficiently positive potential to an oxidized Pt (or carbon) electrode, one promotes the one-electron oxidation of the acid by the Ce^{4+} , creating an intermediate (e.g., $\text{CO}_2^{\cdot-}$) which is a strong reducing agent. This intermediate has a sufficiently long lifetime in aqueous solution to be able to reduce other molecules in the solution (e.g., $\text{Ru}(\text{bpy})_3^{3+}$ in the light-emitting reaction in 1.0 M H_2SO_4). This system can therefore, in principle, be used for electroreductions in aqueous solution under conditions of mild anodic potential and at a Pt electrode.

Acknowledgment. The support of this research by the Army Research Office is gratefully acknowledged.

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Synthesis of "Face to Face" Porphyrin Dimers Linked by 5,15-Substituents: Potential Binuclear Multielectron Redox Catalysts^{1a}

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Abstract: As part of the development of binuclear transition-metal complexes capable of facilitating multielectron redox reactions of small molecules (such as O_2 and N_2), we have devised an efficient and synthetically flexible route to 5,15-disubstituted porphyrins which affords multigram quantities of isomerically pure porphyrins without recourse to chromatography. The 5,15-substituents are principally amine $((\text{CH}_2)_n\text{NHR}$ ($n = 1, 2, 3$; $\text{R} = \text{H}, \text{CH}_3$)) and acid chloride $((\text{CH}_2)_n\text{C}(\text{O})\text{Cl}$ ($n = 1, 2$)) groups. Reactions of the two types of substituted porphyrins lead to a new class of "face to face" porphyrins with interporphyrin amide bridges of varying length (4-7 atoms). An amine-linked dimer has been produced by the reduction of an appropriate amide linkage. Purely hydrocarbon-linked dimers have also been prepared by the direct coupling of bis(dipyrrylmethanes) bridged by aliphatic $(\text{CH}_2)_n$ ($n = 4, 6$) chains. The dimeric porphyrin compounds have been fully characterized by their visible and NMR spectra. The crystal and molecular structure of the bis(copper(II)) complex of one of the amide-linked dimers, the first such determination of a "face to face" porphyrin, is reported. Crystal data for $\text{Cu}_2\text{C}_{74}\text{N}_{10}\text{O}_2\text{H}_{86}\cdot 2\text{H}_2\text{O}\cdot \text{C}_4\text{H}_8$: space group $C_{2h}^2-P2_1/c$; $a = 11.878$ (6) Å, $b = 13.304$ (7) Å, $c = 23.725$ (13) Å, $\beta = 114.60$ (2)° at -140°C ; $Z = 2$. A crystallographic center of symmetry is imposed on the dimer. The structure was refined on all data including $F_o^2 < 0$ (4663 observations) to values for R and R_w on F^2 of 0.103 and 0.152. For the portion of data having $F_o^2 > 3\sigma(F_o^2)$ (3213 observations) the values for R and R_w on F are 0.063 and 0.073. The spectral properties of these new porphyrin dimers are discussed with reference to the structural analysis. A striking feature of the structure is a shear-like displacement of one porphyrin unit with respect to the other by an average distance of 4.95 Å. The Cu...Cu separation is 6.332 (4) Å and the interplanar separation of the two porphyrin rings is 3.87 Å. In solution at ambient temperatures, conformational changes involving motions of the two porphyrin rings cause considerable line broadening in the ^1H NMR spectra of all 5,15-bridged dimers. However, at temperatures above 90°C conformational equilibria are sufficiently rapid to produce well-resolved spectra.

Introduction

We have been interested in the development of new catalysts for the direct, four-electron electrochemical reduction of O_2 to H_2O at potentials approaching the thermodynamic value of +1.23 V (vs. the normal hydrogen electrode). In a broader context such

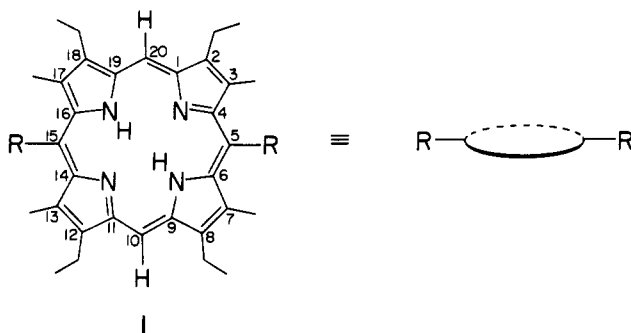
catalysts may also promote multielectron-transfer reactions for other small molecules such as dinitrogen. In a recent paper we discussed our approach to the design of multielectron redox

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(1) (a) For a more detailed treatment of materials in this paper see: Schmittou, Eric R. Ph.D. Dissertation, Stanford University, 1979. (b) Natural Sciences and Engineering Council of Canada Postdoctoral Fellow, 1976-1978. (c) National Science Foundation Predoctoral Fellow, 1973-1976.

catalysts in the form of doubly linked diporphyrins or, more picturesquely, "face to face" porphyrin dimer systems, and we reported the synthesis and characterization of novel "face to face" porphyrin compounds based on functionalized *meso*-tetraphenylporphyrin derivatives.² During the past few years interest has increased in dimeric porphyrins^{3,4} not only as potential redox catalysts^{2,3} but also as models for chlorin aggregates in chlorophylls.⁴

Problems associated with the synthesis of "face to face" porphyrins based on *meso*-tetraphenylporphyrin stimulated us to develop a more efficient and flexible synthetic scheme for the generation of porphyrin dimers with the following features. First, aliphatic as well as aromatic links of variable length and functionality between the porphyrin subunits were sought in order to probe the sensitivity of ligand binding, electrochemical, and spectral properties to the interporphyrin separation and the nature of the links. Second, we wished to control the solubility characteristics of the porphyrins by introducing appropriate alkyl substituents at the β -pyrrolic positions. Third, we wished to generate isomerically pure "face to face" porphyrins in order to simplify characterization. When 5,15-disubstituted porphyrins **1** were synthesized, which are the precursors of the "face to face" porphyrins, both of which have idealized D_{2h} symmetry, the above goals were in part achieved.



We now report the successful synthesis of a variety of "face to face" porphyrin dimers connected at the 5,15-positions by links of varying length and functional type. These compounds have been characterized by the usual spectroscopic and analytical methods, in particular ¹H NMR spectroscopy at elevated temperatures. The structure of the bis(copper(II)) derivative of one representative dimer system has been determined by single-crystal X-ray diffraction methods.

Results and Discussion

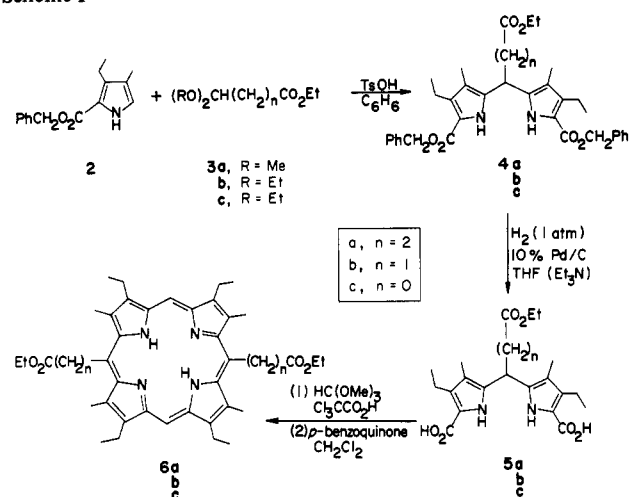
Synthesis. 5,15-Disubstituted porphyrins were synthesized by the coupling of dipyrromethane-5,5'-dicarboxylic acids using trimethyl orthoformate in the presence of trichloroacetic acid followed by athermal or chemical oxidation—a method first reported by Jackson et al. for the preparation of coproporphyrin II.⁵

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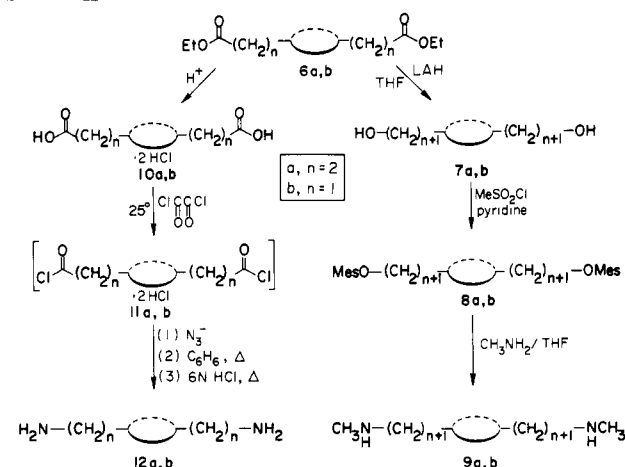
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Scheme I



Scheme II



Dipyrromethane derivatives, bearing functionalized substituents at the methylene bridge carbon atoms, were prepared by the reaction of a 5-unsubstituted pyrrole-2-carboxylic acid benzyl ester with appropriate functionalized aromatic or aliphatic aldehydes and acetals. During the course of this work Baldwin et al.⁶ reported a similar route to 5,15-diarylporphyrins.

5,15-Dialkylporphyrins. In our initial efforts to prepare 5,15-diarylporphyrins, pyrrole precursors with methyl groups at the 3- and 4-positions were used. However, the low solubility of the resulting porphyrins and their tendency to polymerize during attempts to form "face to face" porphyrins forced us to abandon the route.⁷ We therefore turned our attention to 5,15-dialkylporphyrins **1** bearing 2,8,12,18-ethyl substituents, whose solubility characteristics were more satisfactory.

The condensation of 2 mol of benzyl 3-ethyl-4-methylpyrrole-2-carboxylate **2** with an aliphatic ester aldehyde or ester acetal **3** in benzene with *p*-toluenesulfonic acid as catalyst gave alkyl-substituted dipyrromethane dibenzyl esters **4** (Scheme I). The pyrrole **2** was obtained from 5-(carboethoxy)-4-ethyl-3-methylpyrrole-2-carboxylic acid⁹ by the method of Battersby et al.¹⁰ involving iodinate decarboxylation followed by reduction

(5) Jackson, A. H.; Kenner, G. W.; Wass, J. *J. Chem. Soc., Perkin Trans. I* **1972** 1475–1483.

(6) Baldwin, J. E.; Klose, T.; Peters, M. *J. Chem. Soc., Chem. Commun.* **1976**, 881–883.

(7) For the synthesis of ortho- and meta-functionalized 5,15-diarylocta-methylporphyrins, see ref 1a.

(8) Filippovich, E. I.; Evstigneeva, R. P.; Postnikova, G. S.; Palagina, T. A.; Cherkasov, A. N.; Preobrazhenskii, N. A. *Khim. Geterotsikl. Soedin.* **1965**, 728–733.

(9) Archibald, J. L.; Walker, D. M.; Shaw, K. B.; Markovac, A.; MacDonald, S. F. *Can. J. Chem.* **1966**, *44*, 345–362.

with HI. This method is more efficient than the thermal decarboxylation reported by Archibald et al.⁹ Basic transesterification of the ethyl ester gave the benzyl ester **2**. The ester acetal, ethyl 4,4-dimethoxybutyrate (**3a**), was obtained in 90% yield by ozonolysis of ethyl 4-pentenoate¹¹ in methanol. Ethyl propiolate was treated with potassium ethoxide in ethanol to give ethyl 3,3-diethoxypropionate (**3b**) in 100% yield; ethyl diethoxyacetate was obtained commercially.

The dipyrromethane dibenzyl esters **4** were converted quantitatively to their corresponding 5,5'-dicarboxylic acids **5** by hydrogenolysis (H_2 1 atm, 10% Pd/C, THF + Et_3N). The dipyrromethane dicarboxylic acids were then coupled to give the desired 5,15-disubstituted porphyrins **6a-c** in yields of 43%, 52%, and 34%, respectively (Scheme I). Routinely 2–3 g of porphyrins **6a** and **6b** were prepared without need for chromatographic isolation or purification. These porphyrins exhibited satisfactory solubility.

The yields of the porphyrin-forming reactions have been improved by changing the conditions from those reported by Jackson et al.⁵ While our conditions are not rigorously optimized, we have found that treating a 1.2×10^{-2} M CH_2Cl_2 solution of the dipyrromethane dicarboxylic acid with a 10- to 30-fold excess of trimethyl orthoformate and trichloroacetic acid (0.1 M) results in shortened reaction times and affords a doubling of yields over the conditions of Jackson et al.⁵ (50% as opposed to 25%).

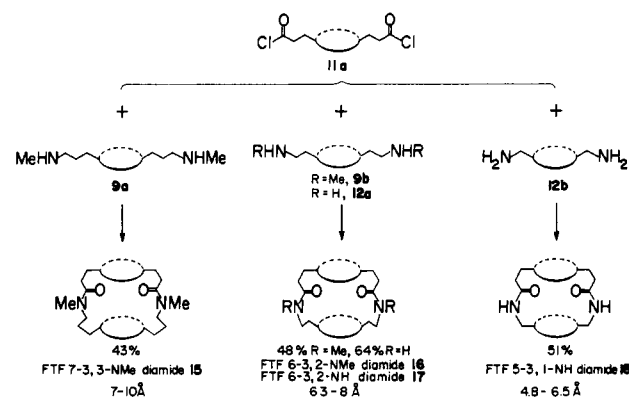
Functional group transformations similar to those reported by Chang and co-workers^{3c,d} together with some other versatile transformations were used to obtain from the diester porphyrins **6a,b** diacid, diacid chloride, diol, dimesylate, diisocyanate, and diamine porphyrins (Scheme II). The diols **7a,b** were obtained by $LiAlH_4$ reduction of the corresponding diesters. Treatment of these diols with methanesulfonyl chloride in pyridine gave the dimesylate porphyrins **8a,b**, useful derivatives for displacement reactions. Secondary diamine porphyrins, the *N*-methyl diamines **9a,b**, were obtained by treating the dimesylates **8a,b** with $MeNH_2$ in THF under pressure. Acidic hydrolysis of the diester porphyrins **6a,b** gave the diacid dihydrochlorides **10a,b**, and these could be converted to the diacid chlorides **11a,b** with oxalyl chloride. Treatment of the diacid chloride porphyrins **11** with azide in methylene chloride gave diacid azide derivatives **13**. Upon being heated in benzene, these were converted to the diisocyanate derivatives **14** which could then be used without isolation to give the primary diamine porphyrins **12a,b** by acid hydrolysis. Both the diacid azide and the diisocyanate derivatives **13b** and **14b**, respectively, were isolated. The solubility of the free base porphyrins was satisfactory. The diamine and diol porphyrins, however, were less soluble than the diester or dimesylate porphyrins perhaps because of hydrogen bonding. In order to manipulate these porphyrins in solution, we added a second solvent component with hydrogen-bonding ability (an alcohol or tertiary amine) to the bulk solvent (usually a chlorinated solvent).

Unfortunately, the diester porphyrin **6c** could not be successfully hydrolyzed to a diacid derivative nor was reduction to a diol derivative with $LiAlH_4$ or with sodium bis(2-methoxyethoxy)-dihydroaluminate successful. It appears that the carbonyl group of the diester is severely shielded by the β -methyl groups of the porphyrin ring.

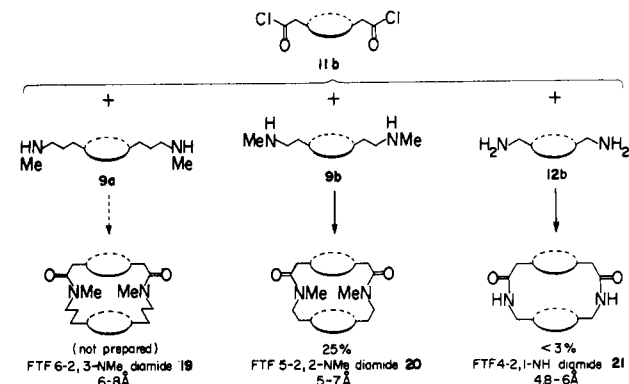
"Face to Face" Porphyrins. With the range of difunctionalized porphyrins described above, several pairwise combinations can be envisioned which could give covalently linked dimers. We have concentrated our efforts on the synthesis of various amide-linked systems. Some evidence has been obtained to suggest the formation of a urea-linked dimer, and, in addition, hydrocarbon-linked dimers have been prepared by using a variation in the general porphyrin synthetic method.

Amide-linked dimers have been prepared from appropriate porphyrin diamines and diacid chlorides such that "face to face" systems are obtained in which the number of atoms in the linkage

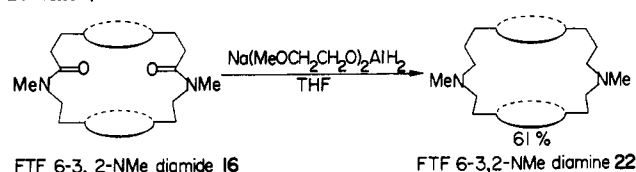
Scheme III



Scheme IV



Scheme V



between meso positions ranges from 7 to 4. The best method we have found for coupling diamine porphyrins with diacid chloride porphyrins is a high dilution technique. The variety of "face to face" systems that we have prepared, along with their respective yields, is shown in Schemes III and IV. Estimates of interplanar distances, with the assumption of a "face to face" orientation, were made with Corey-Pauling-Koltun molecular models. In particular, no attempt was made to prepare FTF 6-2,3-NMe¹² diamide **19** since it was expected to be similar to other FTF **6** systems and to be difficult to prepare. On one occasion the dimer FTF 4-2,1-NH diamide **21** was prepared in extremely low yield and characterized as the Cu(II) complex by IR and field desorption MS. This reaction could not be repeated successfully. Otherwise the "face to face" porphyrins were conveniently prepared in 25–160-mg quantities. The reaction between acid chloride and amine porphyrins is very fast, complete in a minute or less, and does not require the long addition times reported by Chang et al.^{3c,d} The workup and isolation of all these dimers are simple and efficient.

One amine-linked system, the FTF 6-3,2-NMe diamine **22**, was successfully prepared by reducing FTF 6-3,2-NMe diamide **16** (Scheme V). However, attempts similarly to reduce the FTF 5-2,2-NMe diamide **20** led to degradation of the dimer structure and apparent cleavage of the linkage(s). The amine couplings

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(11) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* 1973, 957–960.

(12) The shorthand nomenclature we have chosen for the dimers is of the form: FTF X-Y,Z-NR diamide, diamine, or diurea. Hydrocarbon-linked systems are denoted FTF X-CX. The number "X" represents the total number of atoms in the linkage between the meso positions of the porphyrins. Numbers "Y" and "Z" refer to the number of carbon atoms in the linkage derived from the carboxylic acid and amine side chains, respectively. "R" denotes the remaining group attached to nitrogen.

Table I. Electronic Spectral Data for Free-Base "Face-to-Face" Porphyrins and Selected Single Porphyrins^a (λ_{\max} in nm ($\log \epsilon$)^b)

porphyrin	Soret (V)	visible			
		IV	III	II	I
C3 diester 6a	410 (5.28)	510 (4.14)	545 (3.56)	577 (3.71)	630 (2.80)
C3 diacid 10a		510	545	577	628
C3 NMe diamine 9a	410	511	547	578	630
C2 diester 6b	410 (5.31)	509 (4.18)	544 (3.76)	577 (3.79)	629 (3.23)
C2 diacid 10b	417	510	545	578	630
C2 diamine 12a	413	510	545	578	628
C1 diamine 12b	410	509	544	576	628
C1 diester 6c	400	502	537	572	625
5,15-dimethyloctamethylporphyrin ^c	416 (5.17)	512 (4.06)	547 (3.49)	584 (3.65)	632 (2.82)
5,15-dimethyloctaethylporphyrin ^d	412 (5.29)	513 (4.19)	548 (3.62)	586 (3.72)	636 (2.70)
FTF 7-3,3-NMe diamide 15	403	515	551	583	635
FTF 6-3,2-NMe diamide 16	405	516	554	587	640
FTF 6-3,2-NH diamide 17	408 (5.48)	515 (4.32)	556 (3.93)	584 (3.97)	639 (3.28)
FTF 5-3,1-NH diamide 18	398 (br)	515	555	582	643
FTF 5-2,2-NMe diamide 20	399 (br)	520	559	591	647
FTF 4-2,1-NH diamide 21	395 (br)	515	554	580	645
FTF 6-3,2-NMe diamine 22	408	518	556	589	642
FTF 7-2,2-NH diurea 23	413	516	555	580	630
FTF 6-C6 25a	407 (br)	515	558	587	639
FTF 4-C4 25b	405 (br)	521	561	594	650

^a Solvent is CHCl_3 + 0.5% Et_3N except as noted; porphyrin concentration is about 5×10^{-5} M. ^b Molar extinction coefficients are included for representative single and "face to face" porphyrins and are not expected to differ substantially from these values for unreported systems. ^c In C_6H_6 , ref 13. ^d In dioxane, ref 14.

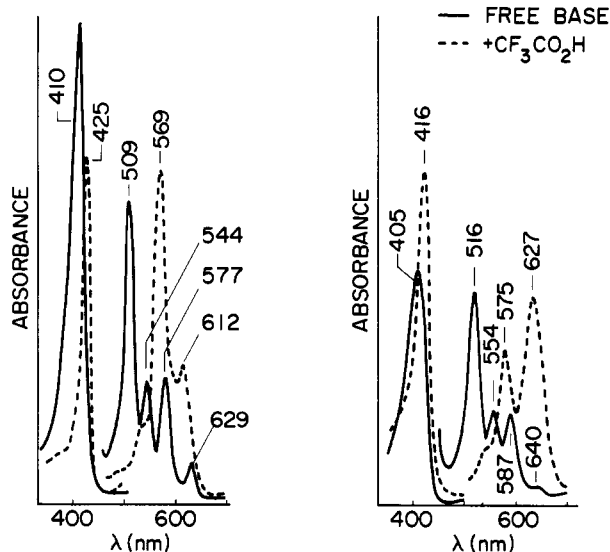
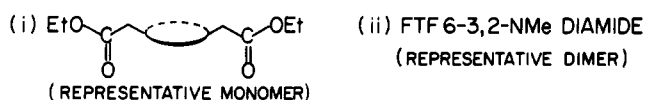


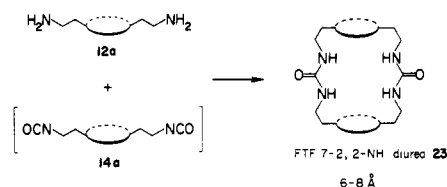
Figure 1. Electronic absorption spectra of a selected porphyrin monomer and dimer ($\sim 10^{-5}$ M in CHCl_3). The Soret absorption is recorded at approximately 10 times the attenuation used for the "visible" bands.

were investigated in the belief that a more flexible linkage between the porphyrins might provide increased freedom of movement of one porphyrin ring with respect to the other. ^1H NMR evidence (vide infra) suggests that the amide-linked systems exhibit very slow interplanar motions and a variety of orientations at ambient temperatures. Unfortunately this is also true for the FTF 6-3,2-NMe diamine 22.

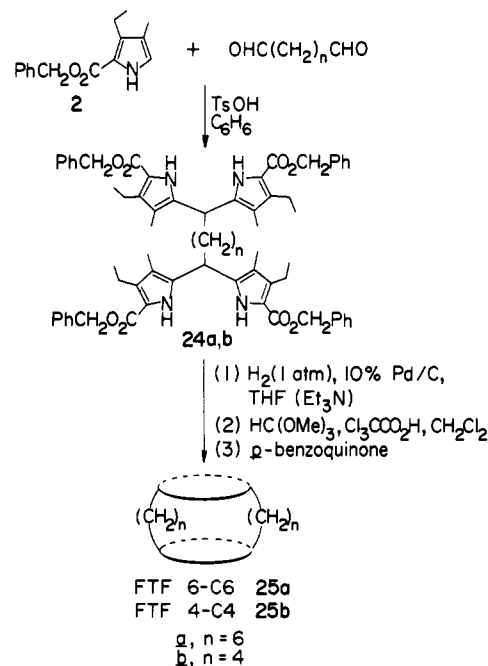
The compound FTF 7-2,2-NH diurea 23 appeared to be obtained on one occasion as a byproduct when the diamine 12a was prepared by the hydrolysis of a diisocyanate porphyrin. It is possible that the combination of an amine porphyrin with an isocyanate porphyrin in the reaction mixture could give a urea-linked dimer 23 (Scheme VI). The UV/vis, IR, MS, and NMR spectral data for this compound support its formulation as a urea-linked dimer.

Using a variation of the porphyrin synthetic scheme, we have prepared and characterized two "face to face" porphyrin dimers

Scheme VI



Scheme VII



linked by aliphatic hydrocarbon bridges. Linkages with six (FTF 6-C6) and four (FTF 4-C4) methylene groups have been introduced. The condensation of the pyrrole 2 with 1,8-octanedial or 1,6-hexanedial (or the acetal equivalents) produced the bis(dipyrromethanes) 24a and 24b, respectively, in about 70% yield. These were treated as shown in Scheme VII to give eventually the alkyl-linked "face to face" porphyrins 25a and 25b in low ($\sim 2\%$) yield. These are the first porphyrin dimers doubly linked by $(\text{CH}_2)_n$ hydrocarbon bridges to be reported.

Table II. Electronic Spectral Data for "Face to Face" Porphyrins and Selected Single Porphyrins in Acidic Media^a (λ_{\max} in nm)

porphyrin	Soret	visible	
C3 diester 6a	428	535 (sh)	572 620
C3 NMe diamine 9a	427	535 (sh)	570 619
C2 diester 6b	425	535 (sh)	569 612
C2 diacid 10b		535 (sh)	569 613
C2 NMe diamine 9b	426	535 (sh)	570 618
C2 diamine 12a	428	535	572 619
C1 diamine 12b	425	540 (sh)	570 617
C1 diester 6c	415	530 (sh)	564 612
5,15-dimethyloctaethylporphyrin ^b	420	530	573 624
FTF 7-3,3-NMe diamide 15	420	541 (sh)	575 628
FTF 6-3,2-NMe diamide 16	416	542 (sh)	575 627
FTF 6-3,2-NH diamide 17	425	547 (sh)	578 634
FTF 5-3,1-NH diamide 18	407 (br)	545 (sh)	572 624
FTF 5-2,2-NMe diamide 20	404	545 (sh)	576 633
FTF 4-2,1-NH diamide 21	408	548 (sh)	576 633
FTF 6-3,2-NMe diamine 22	419	545 (sh)	578 635
FTF 7-2,2-NH diurea 23	420	545 (sh)	574 629
FTF 6-C6 25a	418	545 (sh)	575 632
FTF 4-C4 25b	412	545 (sh)	579 638

^a In CHCl_3 + 0.5% $\text{CF}_3\text{CO}_2\text{H}$ except as noted. ^b In $\text{CF}_3\text{CO}_2\text{H}$, ref 14.

Characterization. Electronic Spectra. The position and intensity patterns of the visible bands for the free-base single 5,15-dialkylporphyrins agree well with the spectra reported for 5,15-dimethyloctamethylporphyrin¹³ and 5,15-dimethyloctaethylporphyrin¹⁴ (Table I and Figure 1). The visible bands have the intensity pattern $\text{IV} > \text{III} < \text{II} > \text{I}$, a so-called *phyllo*-type spectrum, indicative of the presence of one or two meso substituents¹⁵ on an octaalkylporphyrin. The spectra do not appear to be sensitive to the nature of the functional group attached at the meso position as long as some "insulating" methylene groups come between the functional group and the porphyrin. Only with the C1 diester 6c, in which the carbonyl group is directly attached to the meso position, do the positions of the maxima change substantially. The spectra of the 5,15-dialkylporphyrin dications also agree well with that reported for the dication of 5,15-dimethyloctaethylporphyrin (Table II).¹⁴

The "face to face" dimers have distinctly different spectra compared with those for their parent single porphyrins. The visible bands of the free-base dimers are generally shifted to longer wavelength (red-shift) and the Soret band is shifted to shorter wavelength (blue-shift). The bands also appear to be broadened. These features are concentration independent in the concentration range 5×10^{-5} to 5×10^{-6} M. The "face to face" dimers in acidic media also show blue-shifted Soret bands and red-shifted visible bands.

These spectral patterns have been diagnostically useful in determining which products are the "face to face" dimers when new dimer preparations have been tried for the first time and provide one piece of evidence that compounds 21 and 23 are FTF 4-2,1-NH diamide and FTF 7-2,2-NH diurea, respectively. Blue-shifted Soret bands and red-shifted visible bands relative to the monomeric porphyrin have previously been reported for the "face to face" porphyrins of Collman et al.² and Chang and co-workers.^{3c,d} Similar spectral shifts were anticipated for our 5,15-linked octaalkylporphyrins.

While the spectral shifts are qualitatively useful for the identification of dimer compounds, a rigorous explanation for the observed shifts has not been attempted. The problem is confused by the variety of spectral properties reported for other dimer systems. Whereas the singly and doubly linked mesoporphyrin-IX dimers of Ichimura,¹⁶ which are not rigidly constrained to "face

to face" orientations, display blue-shifted Soret bands and red-shifted visible bands, the β,β' -alkyl-linked porphyrin dimers reported by Paine et al.¹⁷ show no spectral shifts when the porphyrin units are separated by more than two methylene groups. The well-defined "face to face" dimer of Kagan et al.^{3a} based on *meso*-tetraphenylporphyrin exhibits a broadened but unshifted Soret band and red-shifted visible bands. The doubly linked "face to face" chlorin system of Wasielewski et al.^{4d} exhibits no spectral shifts at all.

The exciton model¹⁸ has been applied to the spectral properties of some porphyrin and chlorin aggregates, in particular the μ -oxo-scandium(III) dimers of octaethyl- and *meso*-tetraphenylporphyrin.¹⁹ Its application to the "face to face" porphyrins of Chang and co-workers^{3c,d} is hampered by insufficient knowledge of the structure in solution of those "face to face" porphyrins. A similar problem exists here.

¹H Nuclear Magnetic Resonance Spectroscopy. The NMR spectra of the 5,15-dialkyl single porphyrins are consistent with a 5,15-disubstitution pattern. The spectral data given in the Experimental Section agree well with the NMR data reported for 5,15-dimethyloctaethylporphyrin.¹⁴

NMR spectroscopy is a particularly useful technique for establishing the integrity of a "face to face" porphyrin dimer. If one porphyrin ring is positioned atop another, the ring current of this second porphyrin can cause additional shifts of the proton resonances,^{2,3c,d} particularly the pyrrolic NH signals. Their resonances are at higher fields than for the monomers, and the upfield shift arises from the additional shielding effect of the second porphyrin atop the first. With the dimers of Chang and co-workers an increase in the shielding effect occurs as the interporphyrin distance is shortened. Upfield shifts have also been observed for peripheral β -pyrrolic substituents. Wasielewski et al.^{4d} observed shifts of 0.1–0.4 ppm for peripheral substituents of a doubly linked "face to face" chlorin dimer. Since all the substituents are moderately shifted upfield an approximately "face to face" or "center to center" orientation was inferred. In studies of "special pair" chlorophyll models, dramatic shifts of specific peripheral substituents indicate that "offset" aggregates are present.^{4b,c} Moderate upfield shifts for all peripheral substituents have been observed for some free-base porphyrins²⁰ and metalloporphyrins²¹ under conditions in which intermolecular aggregation occurs. A mercury(II) octaethylporphyrin "sandwich" complex has shown similar effects.²² The spectral data for this complex are consistent with the formation of dimer aggregates with "center to center" orientations of the porphyrin monomers.

The NMR spectra of the 5,15-dialkylporphyrin dimers and of a representative single porphyrin were recorded under controlled temperature conditions. The chemical shifts of the internal NH, $\beta\text{-CH}_2\text{CH}_3$, $\beta\text{-CH}_3$, and 10,20-H groups are listed in Table III. We find that the spectra of porphyrin monomers and dimers at both room temperature and elevated temperature are invariant to concentration changes from 1×10^{-2} to 2.5×10^{-3} M, in contrast to the easily detected shifts observed for coporphyrins.²⁰ These concentrations are about one-tenth those used in the coporphyrin study. Thus the differences in the chemical shifts observed for these new "face to face" dimers compared with those for the monomers arise from intramolecular effects and not from aggregation. The spectra of the dimers, however, are strongly temperature dependent in contrast to the C3 diester monomer 6a.

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Table III. ^1H NMR Chemical Shifts for Selected Protons in Porphyrin Monomers and Dimers at Elevated Temperatures

porphyrin ^b	temp, °C	chem shifts, ^a δ			
		internal NH, s	$\beta\text{-CH}_2\text{CH}_3$, t	$-\text{CH}_3$, s	meso
C3 diester 6a	90	-1.77	1.84	3.62	10.06
FTF 7-3,3-NMe diamide 15	90	-3.01	1.66, 1.69	2.86, ^c 3.04 ^c	9.45, 9.54
FTF 6-3,2-NMe diamide 16	90	-2.32	1.56, 1.61	3.30, 3.32	9.32, 9.39
FTF 6-3,2-NH diamide 17	90	-2.11	^c	^c	9.57, 9.60
FTF 6-3,2-NH diamide 17	120	-2.02	1.73, 1.75	^c	9.57, 9.60
FTF 6-3,2-NMe diamine 22	90	-2.27	1.58	3.32, 3.36	9.37, 9.45
FTF 5-3,1-NH diamide 18	90	-2.97	1.52, 1.62	3.35, 3.42	9.10, 9.38
FTF 5-2,2-NMe diamide 20	90	^d	1.49, 1.56	3.24, 3.28	9.22, 9.36
FTF 5-2,2-NMe diamide 20	60	-2.97, -3.24	1.46, 1.53	3.24, 3.29	9.21, 9.39
FTF 6-C6 25a	90	^d	1.57	3.27	9.34
FTF 4-C4 25b	90	^d	1.54	3.30	9.07

^a Measured with reference to $\text{Cl}_2\text{CHCDCl}_2$, set at 5.94 vs. Me_4Si , on Varian XL-100 FT NMR. ^b Porphyrin concentration is 1×10^{-2} – 2.5×10^{-3} M in Cl_2DCCl_2 . ^c Broad and poorly resolved. ^d Too broad to detect.

For comparison of dimer and monomer spectra, a temperature of 90 °C or higher is necessary to produce dimer spectra with resolved signals which do not shift or display improved resolution at higher temperatures. A temperature of 90 °C is generally satisfactory, although even at this temperature not all dimers exhibit sharp spectra.

On the other hand, the NMR spectrum of the C3 diester porphyrin monomer 6a shows little temperature dependence. Only the internal NH protons are markedly affected, moving downfield as the temperature is increased from 30 °C to 90 °C. Table III gives NMR data at 90 °C; at this temperature the $\beta\text{-CH}_2\text{CH}_3$, $\beta\text{-CH}_3$, and 10,20-H are unshifted from their positions at 30 °C.

The various "face to face" porphyrins exhibit different temperature effects. Only FTF 5-3,1-NH diamide 18 and FTF 7-2,2-NH diurea 23 exhibit sharp and resolved signals at 30 °C. FTF 5-2,2-NMe diamide 20 requires a temperature of 90 °C to give a sharp spectrum unaffected by further temperature increases. In contrast, FTF 7-3,3-NMe diamide 15 and FTF 6-3,2-NH diamide 17 do not give fully resolved spectra even at 120 °C. Conformational flexibility therefore appears to be dependent on the nature and length of the bridging unit.

In spite of the complex temperature dependence of the various "face to face" dimers, the spectra obtained at 90 °C which show sharpened signals for the $\beta\text{-CH}_2\text{CH}_3$, $\beta\text{-CH}_3$, and 10,20-H groups display other features which are consistent with a dimer formulation. All the amide-linked dimers show two singlets of equal magnitude for the 10,20-H protons indicating the inequivalence of the porphyrin rings joined by unsymmetrical linkages. These signals are not shifted further at temperatures above 90 °C. The dimer 10,20-H resonances are shifted upfield by 0.5–1.0 ppm, and the largest shifts are displayed by dimers with the shortest linkages. This is consistent with the presence of one porphyrin in the vicinity of and generally situated on top of the other porphyrin. The $\beta\text{-CH}_3$ groups appear similarly as two equally intense singlets shifted upfield relative to the $\beta\text{-CH}_3$ resonance of the C3 diester monomer 6a. The $\beta\text{-CH}_2\text{CH}_3$ signals appear as two equally intense triplets (except for FTF 6-3,2-NMe diamine), also shifted upfield. These upfield shifts and the appearance of two signals for each type of proton support the dimer formulation. Finally, the internal NH protons, the chemical shifts of which are very sensitive to temperature, are moved upfield in the dimer systems relative to the monomer porphyrin. The increased shielding generally observed for internal and peripheral protons and the doubling of signals for the selected peripheral substituents are also consistent with the dimer formulation. The NMR spectrum of a representative porphyrin dimer, FTF 6-3,2-NMe diamide 16, is shown in Figure 2.

The formulation of the FTF 7-2,2-NH diurea 23 as a "face to face" compound is suggested by its NMR spectrum, which was obtained only at 30 °C. In accord with the presence of a symmetric bridging unit, the $\beta\text{-CH}_2\text{CH}_3$, $\beta\text{-CH}_3$, and meso-H protons appear as only one triplet, singlet, and singlet, respectively. All are upfield shifted, as is the internal NH signal, by amounts similar to the shifts observed for other dimers. Similar observations were also made for the symmetrical hydrocarbon-linked compounds

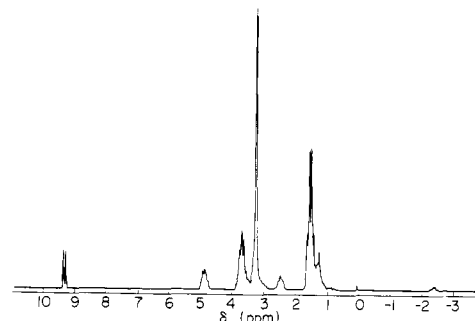


Figure 2. 100-MHz ^1H NMR spectrum of FTF 6-3,2-NMe diamide 16 at 90 °C in Cl_2DCCl_2 .

FTF 6-C6 25a and FTF 4-C4 25b when spectra were recorded at 90 °C.²³

Electron Paramagnetic Resonance Spectroscopy. We have examined the EPR spectra of Cu(II) and Co(II) complexes of the "face to face" porphyrins in the expectation that analyses of the resulting triplet state spectra would provide estimates of metal-metal distances. Such analyses have been successful with other "face to face" porphyrin systems.^{2,3df} Unfortunately, the EPR spectra for these new dimers are complex and do not provide straightforward structural information. At present we do not understand the reasons for the complexities, although variable interplanar orientations may play a part. When we understand better the metal-metal interactions of these systems, the EPR behavior will be discussed in a future report.

X-ray Crystal Structure of the Cu(II) Complex of FTF 6-3,2-NH Diamide 17. While other methods of characterization, most notably elemental analysis and spectroscopy (NMR, IR, MS), support the identification of the meso-linked "face to face" dimers, the unexpected NMR and EPR behavior of some of these systems suggested that a more detailed structural analysis of a dimer was essential. As a representative example of a "face to face" porphyrin, satisfactory crystals of the compound presumed to be the bis(copper(II)) complex of the FTF 6-3,2-NH diamide 17 were prepared.

Although the precision of the analysis of the structure is compromised by disorder and/or high thermal motion, the complex formulated as $\text{Cu}_2(\text{FTF 6-3,2-NH diamide})$ is indeed a porphyrin dimer linked at the 5,15-positions by amide linkages. The crystals studied are the dihydrate monotonolene solvate. As a consequence of a crystallographically imposed center of symmetry, the amide groups are disordered. This disorder, which could be partially resolved, appears to manifest itself in much of the rest of the structure since the thermal motions of many atoms are anomalously high considering the data were collected at -140 °C.

Molecular Packing. Figure 3 shows the atom-labeling scheme for the dimer. The crystal structure appears to be dominated by

(23) While the discussion has focused on comparisons of chemical shifts of selected porphyrin substituents, some of the other proton types in "face to face" dimers have been observed. See Experimental Section.

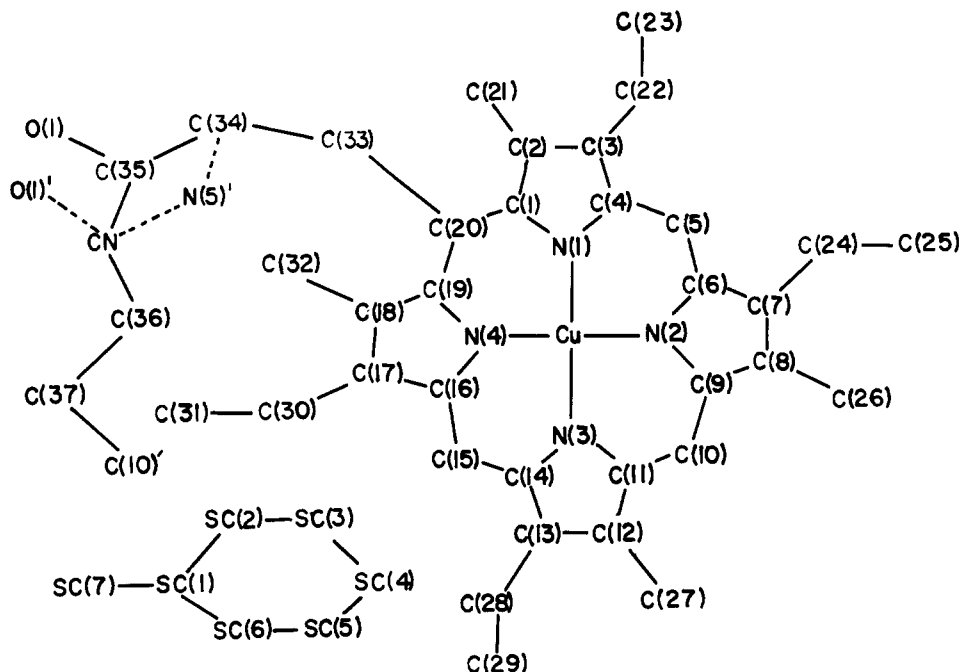


Figure 3. Atom-labeling scheme for $\text{Cu}_2(\text{FTF } 6\text{-}3,2\text{-NH diamide})$. The disordered amide linkage is indicated.

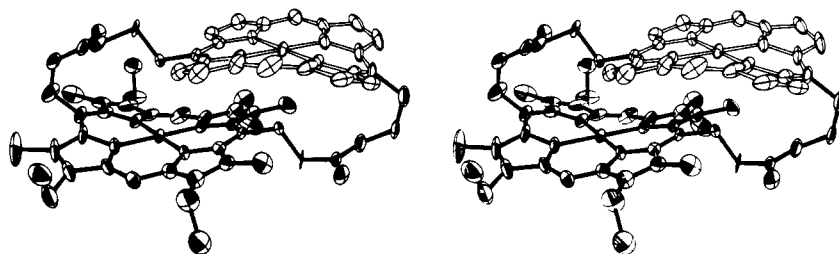


Figure 4. Stereodiagram of $\text{Cu}_2(\text{FTF } 6\text{-}3,2\text{-NH diamide})$. The ethyl and methyl substituents on the unshaded porphyrin ring are omitted for clarity. A center of inversion relates one porphyrin unit to the other. The disorder of the amide group is omitted. Thermal ellipsoids are drawn at the 55% probability level.

nonbonded aromatic type interactions among porphyrin macrocycles and toluene solvate molecules. The two octaalkylporphyrin units are linked, in the notation of Figure 3, at the 10,20 (*meso*)-positions by two amide chains six atoms long. Rather than adopting a "face to face" conformation with both copper ions lying on the normal to the porphyrinato skeleton and with a large empty space between the two macrocycles, there is a shear-like displacement of one porphyrinato unit with respect to the other resulting in a close approach of the two macrocycles (Figure 4). The shear line is almost parallel to the $\text{C}(10)\text{--}\text{C}(20)$ vector. In this conformation aromatic stacking is maximized. Selected intramolecular contacts are given in Table IV.²⁴ The closest contact between atoms of the 24-atom porphyrinato skeletons is 3.46 (1) Å ($\text{C}(1)\cdots\text{C}(19)$). There is a close contact between carbon atom $\text{C}(33)$ of the linking group and the copper ion of 3.174 (7) Å; one hydrogen atom attached to atom $\text{C}(33)$ is only 2.80 Å from the copper ion. The shear displacement along the $\text{C}(10)\text{--}\text{C}(20)$ vector displaces the copper ions in this direction by 4.95 Å. On the basis of this and the known intramolecular copper–copper distance of 6.332 (4) Å, the copper ions are separated by 3.95 Å in the direction normal to the porphyrin planes. Since the copper ions are displaced about 0.04 Å out of the porphyrin planes, the 24-atom porphyrin planes are separated by an average distance of 3.87 Å. This interplanar separation is similar in magnitude to the intermolecular separations found for other crystalline octaalkylporphyrin monomers.^{25,26}

The "sheared" conformation observed here for FTF 6-3,2-NH diamide 17 was totally unexpected. However, the curious NMR properties of this dimer system are perhaps explicable on this basis. For the free-base FTF 6-3,2-NH diamide 17 the NMR signals for the characteristic $\beta\text{-CH}_3$, $\beta\text{-CH}_2\text{CH}_3$, and *meso*-H groups are not resolved. At room temperature only broad and generally unassignable signals are observed. If in solution the free-base dimer assumes an average intramolecular orientation similar to that for the $\text{Cu}(\text{II})$ dimer complex in the solid state, then it appears that even at 120 °C the motions of the amide linkages are too hindered and sluggish to result in a thermally averaged magnetic environment for each porphyrin and yet at room temperature the dimer does not appear to exist in a single locked conformation since NMR line widths are very broad. Thus over a wide temperature range the intramolecular motions are slow and complex. The approximate enthalpy of $\pi\text{-}\pi$ aggregation for porphyrins^{20,21} (-1 to -5 kcal mol^{-1}) is too small to be responsible for this intramolecular effect. An inspection of molecular models of the shear-displaced dimer structure suggests that rapid interconversion of amide linkage conformations might be difficult, particularly if the amide grouping, $-\text{CH}_2\text{C}(\text{O})\text{--}\text{N}(\text{H})\text{--}\text{CH}_2-$, remains approximately planar, as observed in the crystal structure.

The *intermolecular* packing, illustrated in Figure 5, features partial stacking of porphyrin macrocycles with each other and with the toluene solvate molecules. Numerous contacts at approximately van der Waals' separations exist (see Tables V and VI).²⁴ There is a water molecule hydrogen bonded to the carbonyl oxygen atom of each amide linkage. The crystal packing appears

(24) Supplementary material.

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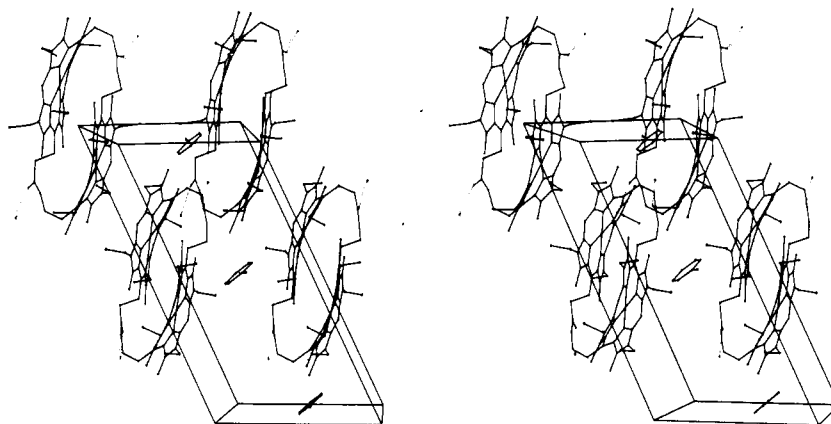


Figure 5. Stereodiagram illustrating the packing of $\text{Cu}_2(\text{FTF } 6-3,2\text{-NH diamide})$ units with the toluene and water solvate molecules. The disorder of the amide and toluene moieties about the inversion center is omitted for clarity.

Table VII. Bond Distances (in Å) for $\text{Cu}_2(\text{FTF } 6-3,2\text{-NH diamide}) \cdot 2\text{H}_2\text{O} \cdot \text{C}_7\text{H}_8$

atoms	distance	average ^a	atoms	distance	average ^a
Cu-N(1)	1.975 (4)	Cu-N _p 1.987 (8)	C(4)-C(5)	1.407 (9)	C _a -C _m 1.394 (17)
Cu-N(2)	1.992 (4)		C(5)-C(6)	1.364 (9)	
Cu-N(3)	1.988 (5)		C(9)-C(10)	1.403 (9)	
Cu-N(4)	1.992 (4)		C(10)-C(11)	1.391 (9)	
N(1)-C(1)	1.405 (7)	N _p -C _a 1.381 (17)	C(14)-C(15)	1.390 (9)	C _b -C _β 1.510 (9)
N(1)-C(4)	1.362 (7)		C(15)-C(16)	1.378 (8)	
N(2)-C(6)	1.378 (8)		C(19)-C(20)	1.417 (7)	
N(2)-C(9)	1.374 (7)		C(20)-C(1)	1.399 (8)	
N(3)-C(11)	1.405 (7)	C _a -C _b 1.446 (16)	C(2)-C(21)	1.507 (9)	C _β -C _γ 1.506 (23)
N(3)-C(14)	1.363 (8)		C(3)-C(22)	1.516 (9)	
N(4)-C(16)	1.372 (7)		C(7)-C(24)	1.515 (10)	
N(4)-C(19)	1.390 (7)		C(8)-C(26)	1.524 (9)	
C(1)-C(2)	1.470 (8)	C _b -C _β 1.350 (8)	C(12)-C(27)	1.508 (9)	
C(3)-C(4)	1.418 (9)		C(13)-C(28)	1.506 (10)	
C(6)-C(7)	1.444 (8)		C(17)-C(30)	1.492 (9)	
C(8)-C(9)	1.462 (9)		C(18)-C(32)	1.513 (8)	
C(11)-C(12)	1.446 (9)	C _b -C _β 1.350 (8)	C(22)-C(23)	1.474 (11)	
C(13)-C(14)	1.445 (8)		C(24)-C(25)	1.524 (9)	
C(16)-C(17)	1.432 (8)		C(28)-C(29)	1.522 (10)	
C(18)-C(19)	1.448 (7)		C(30)-C(31)	1.503 (10)	
C(2)-C(3)	1.356 (9)	C _b -C _β 1.350 (8)	C(10)-C(37)	1.515 (8)	
C(7)-C(8)	1.341 (10)		C(20)-C(33) ^c	1.522 (7)	
C(12)-C(13)	1.346 (10)		C(33)-C(34)	1.569 (8)	
C(17)-C(18)	1.358 (8)		C(34)-C(35)	1.627 (14)	
C(35)-O(1)	1.238 (19)		N(5)-CN ^c	1.179 (10)	
C(35)-CN	1.214 (2)		CN-O(1) ^c	1.500 (14)	
CN-C(36)	1.417 (8)		O-O(1)	2.661 (13) ^b	
C(36)-C(37)	1.371 (9)		O-O(1) ^c	2.746 (13) ^b	
C(34)-N(5) ^c	1.579 (12)		O-N(5) ^c	2.846 (11) ^b	

^a The estimated standard deviation in parentheses is the larger of that calculated for an individual parameter from the inverse matrix or that calculated for an individual observation on the assumption that the values averaged are from the same population. ^b Hydrogen bonds.

^c Primed and unprimed atoms with the same label are related by the crystallographic center of symmetry.

to be facilitated by a two-up two-down arrangement of the β -ethyl substituents. The closest intermolecular Cu-Cu separation is 8.760 (4) Å.

The Coordination Sphere and Porphyrin Stereochemistry. The accommodation of two meso substituents on an already sterically crowded tetramethyltetraethylporphyrin destroys the approximately tetragonal symmetry common to most other metalloporphyrin structures.²⁷ Bond distances and bond angles are listed in Tables VII and VIII, respectively. The average Cu-N_p separation, 1.987 (8) Å, is not significantly different from that observed for Cu(TPrP), 1.999 (5) Å.^{28,29} For the related 5,10-meso-substituted derivative of Cu(OEP), Cu(5,10-RR'-OEP),^{25,29} the Cu-N_p bond lengths range from 1.92 (1) to 2.05 (1) Å.

While the averaged bond parameters, also listed in Tables VII and VIII, are typical of metalloporphyrin structures,²⁷ there is a marked compression to rectangular (and idealized C_{2v}) symmetry along the line C(10)-C(20). With one exception, bond angles may be divided into two sets. The N(2)-Cu-N(3) and N(4)-Cu-N(1) bond angles are less than 90°; the other pair are greater than 90°. This distortion is transmitted to bond angles of the type Cu-N_p-C_a, C_b-C_a-C_m, and C_a-C_m-C_a which may be divided into two sets. With reference to Figure 3, the set of angles typified by Cu-N(1)-C(1) is larger than average; similarly, the type C(2)-C(1)-C(20) is also larger than average, while the two bond angles of the type C(1)-C(20)-C(19) are compressed. Angles of the type N_p-C_a-C_m remain constant. This particular arrangement helps minimize contacts between the methyl substituents on the pyrrole rings and the meso substituents. Close contacts are further ameliorated by opening up the C_a-C_b-C_{Me} bond angles compared with the C_a-C_b-C_{Et} angles. Nonetheless, close 1,4 contacts persist such as those of 3.023 (9) Å between atoms C(21) and C(33) and atoms C(32) and C(33) (Table IV²⁴).

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(29) TPrP = 5,10,15,20-tetrapropylporphyrinato; 5,10-RR'-OEP is an abbreviation for 2,3,7,8,12,13,17,18-octaethyl-5-(2,2-bis((benzyloxy)-carbonyl)vinyl)-10-formylporphyrinato.

Table VIII. Bond Angles (Deg) for $\text{Cu}_2(\text{FTF } 6-3,2\text{-NH diamide})\cdot 2\text{H}_2\text{O}\cdot\text{C}_6\text{H}_5^a$

atoms	angle	average	atoms	angle	average
N(1)-Cu-N(2)	92.3 (2)	$\text{N}_\text{p}-\text{Cu}-\text{N}_\text{p}$ 90.0 (25)	C(4)-C(5)-C(6)	126.9 (6)	$\text{C}_\text{a}-\text{C}_\text{m}-\text{C}_\text{a}$ 125.0 (19)
N(2)-Cu-N(3)	87.4 (2)		C(9)-C(10)-C(11)	122.5 (5)	
N(3)-Cu-N(4)	91.9 (2)		C(14)-C(15)-C(16)	126.1 (6)	
N(4)-Cu-N(1)	88.4 (2)		C(19)-C(20)-C(1)	124.6 (5)	
N(1)-Cu-N(3)	179.7 (2)	$\text{Cu}-\text{N}_\text{p}-\text{C}_\text{a}$ 127.0 (21)	C(9)-C(10)-C(37)	119.4 (7)	$\text{C}_\text{a}-\text{C}_\text{m}-\text{C}$ 118.1 (9)
N(2)-Cu-N(4)	179.3 (2)		C(11)-C(10)-C(37)	117.6 (7)	
Cu-N(1)-C(1)	128.8 (4)		C(19)-C(20)-C(33')	117.6 (5)	
Cu-N(1)-C(4)	125.6 (4)		C(1)-C(20)-C(33')	117.8 (5)	
Cu-N(2)-C(6)	124.9 (4)		C(20)-C(33)-C(34)	114.0 (4)	$\text{C}_\text{a}-\text{C}_\text{b}-\text{CCH}_3$ 130.5 (11)
Cu-N(2)-C(9)	128.8 (4)		C(33)-C(34)-C(35)	105.9 (6)	
Cu-N(3)-C(11)	128.5 (4)		C(34)-C(35)-CN	114.6 (10)	
Cu-N(3)-C(14)	125.1 (4)		C(34)-C(35)-O(1)	128.9 (11)	
Cu-N(4)-C(16)	124.6 (4)	$\text{C}_\text{a}-\text{N}_\text{p}-\text{C}_\text{a}$ 105.9 (5)	O(1)-C(35)-CN	116.5 (13)	$\text{C}_\text{b}-\text{C}_\text{b}-\text{CCH}_3$ 122.0 (5)
Cu-N(4)-C(19)	129.8 (4)		C(35)-CN-C(36)	145.3 (10)	
C(1)-N(1)-C(4)	105.5 (5)		CN-C(36)-C(37)	126.4 (6)	
C(6)-N(2)-C(9)	106.1 (5)		C(36)-C(37)-C(10)	116.4 (6)	$\text{C}_\text{a}-\text{C}_\text{b}-\text{CCH}_2$ 124.8 (10)
C(11)-N(3)-C(14)	106.4 (5)	$\text{N}_\text{p}-\text{C}_\text{a}-\text{C}_\text{b}$ 109.7 (12)	C(33)-C(34)-N(5')	103.8 (5)	
C(16)-N(4)-C(19)	105.5 (4)		C(34)-N(5')-CN	120.3 (9)	
N(1)-C(1)-C(2)	108.3 (5)		N(5')-CN-O(1')	116.9 (9)	
N(1)-C(4)-C(3)	112.0 (5)	$\text{C}_\text{a}-\text{C}_\text{b}-\text{C}_\text{b}$ 107.2 (5)	N(5')-CN-C(36)	142.1 (9)	$\text{C}_\text{b}-\text{C}_\text{b}-\text{CCH}_2$ 128.2 (12)
N(2)-C(6)-C(7)	110.1 (6)		O(1')-CN-C(36)	100.9 (8)	
N(2)-C(9)-C(8)	109.2 (6)		C(1)-C(2)-C(21)	131.4 (6)	
N(3)-C(11)-C(12)	108.2 (6)		C(9)-C(8)-C(26)	130.3 (8)	$\text{C}_\text{b}-\text{CCH}_2-\text{CCH}_3$ 111.6 (7)
N(3)-C(14)-C(13)	110.2 (6)	$\text{N}_\text{p}-\text{C}_\text{a}-\text{C}_\text{m}$ 124.1 (8)	C(11)-C(12)-C(27)	129.0 (8)	
N(4)-C(16)-C(17)	110.2 (5)		C(19)-C(18)-C(32)	131.2 (6)	
N(4)-C(19)-C(18)	109.3 (5)		C(3)-C(2)-C(21)	121.7 (6)	
C(1)-C(2)-C(3)	106.8 (6)	$\text{C}_\text{b}-\text{C}_\text{a}-\text{C}_\text{m}$ 125.9 (20)	C(7)-C(8)-C(26)	122.3 (7)	$\text{C}_\text{b}-\text{CCH}_2-\text{CCH}_3$ 111.6 (7)
C(2)-C(3)-C(4)	107.2 (5)		C(13)-C(12)-C(27)	122.6 (7)	
C(6)-C(7)-C(8)	107.0 (6)		C(17)-C(18)-C(32)	121.4 (5)	
C(7)-C(8)-C(9)	107.3 (6)		C(4)-C(3)-C(22)	125.3 (7)	
C(11)-C(12)-C(13)	108.1 (6)	$\text{C}_\text{b}-\text{C}_\text{a}-\text{C}_\text{m}$ 125.9 (20)	C(6)-C(7)-C(24)	125.6 (7)	$\text{C}_\text{b}-\text{CCH}_2-\text{CCH}_3$ 111.6 (7)
C(12)-C(13)-C(14)	106.9 (6)		C(14)-C(13)-C(28)	123.3 (7)	
C(16)-C(17)-C(18)	106.5 (5)		C(16)-C(17)-C(30)	124.9 (6)	
C(17)-C(18)-C(19)	107.4 (5)		C(2)-C(3)-C(22)	127.3 (7)	
N(1)-C(1)-C(20)	123.9 (5)	$\text{N}_\text{p}-\text{C}_\text{a}-\text{C}_\text{m}$ 124.1 (8)	C(8)-C(7)-C(24)	127.2 (6)	$\text{C}_\text{b}-\text{CCH}_2-\text{CCH}_3$ 111.6 (7)
N(1)-C(4)-C(5)	124.1 (6)		C(12)-C(13)-C(28)	129.7 (6)	
N(2)-C(6)-C(5)	124.4 (5)		C(18)-C(17)-C(30)	128.6 (6)	
N(2)-C(9)-C(10)	123.6 (6)		C(3)-C(22)-C(23)	111.7 (7)	
N(3)-C(11)-C(10)	123.6 (6)	$\text{C}_\text{b}-\text{C}_\text{a}-\text{C}_\text{m}$ 125.9 (20)	C(7)-C(24)-C(25)	111.7 (6)	$\text{C}_\text{b}-\text{CCH}_2-\text{CCH}_3$ 111.6 (7)
N(3)-C(14)-C(15)	124.6 (5)		C(13)-C(28)-C(29)	110.7 (6)	
N(4)-C(16)-C(15)	125.4 (6)		C(17)-C(30)-C(31)	112.1 (7)	
N(4)-C(19)-C(20)	122.5 (5)				
C(2)-C(1)-C(20)	127.8 (5)				
C(3)-C(4)-C(5)	123.5 (6)				
C(7)-C(6)-C(5)	125.1 (6)				
C(8)-C(9)-C(10)	126.6 (6)				
C(12)-C(11)-C(10)	128.1 (6)				
C(13)-C(14)-C(15)	124.8 (6)				
C(17)-C(16)-C(15)	123.2 (5)				
C(18)-C(19)-C(20)	128.1 (5)				

^a See footnotes to Table VII.

The internal bond angles of the pyrrole rings exhibit no significant scatter about their mean with respect to the estimated standard deviation of an individual bond angle for a given class of angles. Three of the four pyrrole rings show small, but significant, departures from planarity (Table IX). Yet there is an apparently significant scatter in bond lengths about their mean value for each class of porphyrinato bonds except for the $\text{C}_\text{b}-\text{C}_\text{b}$ class. The porphyrinato skeleton is substantially buckled. Dihedral angles of up to 23.8° are observed between adjacent pyrrole rings (Table X) and the meso substituent C(37) lies an extraordinarily large 1.550 \AA out of the least-squares plane of the porphyrinato skeleton (Figure 6). Hence, some electronic distortions are possible such as have been deduced on the basis of its UV-visible spectral properties²⁵ for the similarly buckled $\text{Cu}(5,10\text{-RR}'\text{-OEP})$ molecule, although their rather large estimated standard deviations mask any pattern in bond parameters which might be attributed to the substituents. There is, however, no discernible pattern in the scatter of the porphyrinato bond lengths in the present structure. Therefore, in view of the anomalously high thermal motion afflicting many parts of the structure, probably more accurately described as a small, unresolvable disorder, we are reluctant to ascribe the observed scatter to a real electronic effect

arising from the severe distortion from planarity of the macrocycle. The magnitude of the buckling deformation is similar to that observed for $\text{Cu}(5,10\text{-RR}'\text{-OEP})$.²⁵ The porphyrinato skeleton takes on a ruffled shape in which the meso carbon atoms are found to lie alternately from 0.35 to 0.65 \AA above and below the least-squares porphyrin plane. This deformation appears to minimize steric interactions between β -methyl groups and meso substituents. A meso carbon atom displacement of $0.4\text{--}0.5 \text{ \AA}$ may result from steric effects in a single porphyrinato unit, taking $\text{Cu}(5,10\text{-RR}'\text{-OEP})$ as a model. The effects of dimer molecular packing, especially the conformations of the amide groups, may be responsible for meso carbon atom displacements outside this range. Particularly noteworthy is the $0.648 (6) \text{ \AA}$ displacement of atom C(10). Although affected by both resolved and unresolved disorder, the amide groups do appear to be approximately planar (see Table IX). Furthermore the torsional angles, $\text{C}(34)\text{--C}(35)\text{--CN--C}(36)$ and $\text{C}(34)\text{--N}(5')\text{--CN--C}(36)$ which are $172.0 (9)^\circ$ and $-171.9 (8)^\circ$, respectively, are close to the 180° expected for a planar amide group. This planarity of the amide groups is responsible, at least in part, not only for the observed "sheared" conformation of the porphyrin dimer but also for the "slow" conformational equilibria detected by NMR spectroscopy.

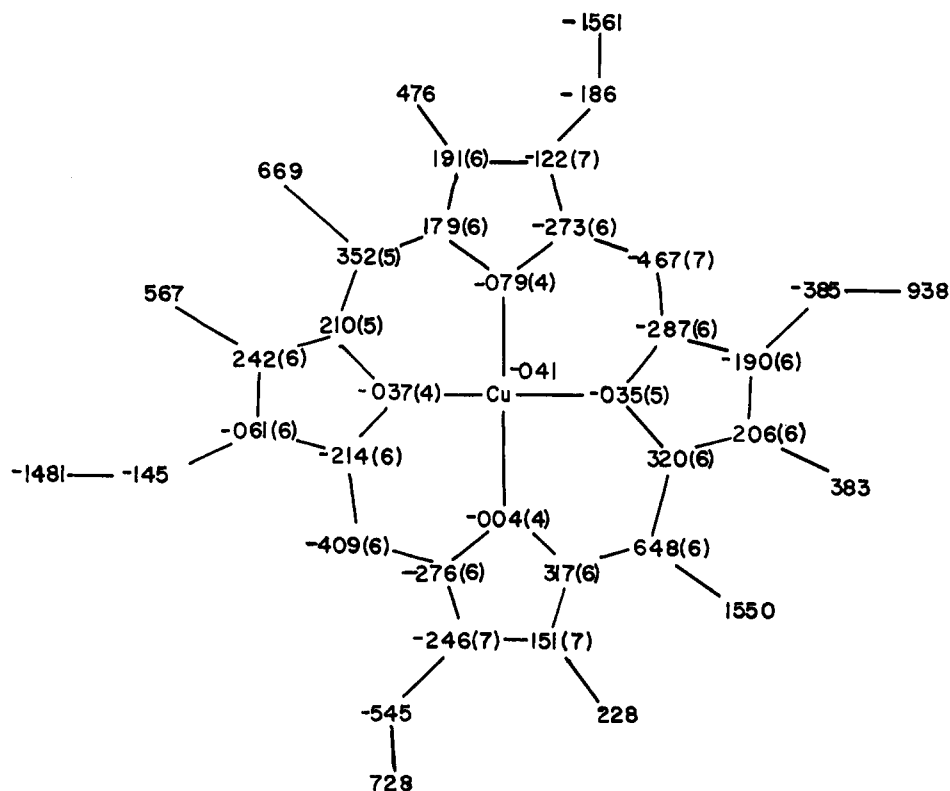


Figure 6. Displacements of atoms ($\text{\AA} \times 10^3$) from the least-squares plane of the 24-atom porphyrinato skeleton. Estimated standard deviations in parentheses are given for only those atoms included in the calculation of the plane. The orientation of the molecule is that depicted in Figure 3.

Table IX. Least-Squares Planes for Cu_2 (FTF 6-3,2-NH diamide)^a

name	$Ax + By + Cz - D = 0$				atoms in plane displacement ^b				other atoms displacement
	A	B	C	D					
I	11.339	-0.877	-15.694	-1.971	N(1)	N(2)	N(3)	N(4)	Cu
II	11.292	-0.688	-15.988	-1.88 (5)	-2 (4)	3 (5)	-3 (5)	2 (4)	-2
pyrrole-1	11.769	-1.500	-11.392	-1.599	C(5)	C(10)	C(15)	C(20)	Cu
pyrrole-2	10.223	-3.595	-17.813	-2.444	-556 (7)	483 (6)	-474 (6)	365 (5)	-118
pyrrole-3	10.317	1.022	-18.942	-2.203	N(1)	C(1)	C(2)	C(3)	C(4)
pyrrole-4	11.762	1.023	-12.295	-1.564	8 (4)	-16 (6)	18 (6)	-10 (7)	-6 (6)
amide-1	11.692	2.154	-8.220	3.549	N(2)	C(6)	C(7)	C(8)	C(9)
amide-2	11.787	1.098	-7.823	3.613	-17 (5)	28 (6)	-18 (6)	2 (6)	17 (6)
porphyrin	11.385	-0.666	-15.522	-1.897	N(3)	C(11)	C(12)	C(13)	C(14)
					-18 (5)	14 (6)	5 (7)	-24 (6)	30 (6)
					N(4)	C(16)	C(17)	C(18)	C(19)
					9 (4)	-2 (6)	-13 (6)	19 (6)	-18 (5)
					C(34)	C(35)	O(1)	CV	C(36)
					-15	-9	-10	39	-39
					C(34)	N(5')	CN	O(1')	C(36)
					-32	61	28	72	-52
					See Figure 6				

^a The plane is in crystal coordinates as defined by W. C. Hamilton (*Acta Crystallogr.* 1961, 14, 185-189). ^b The displacement is in $\text{\AA} \times 10^3$.

Table X. Dihedral Angles (Deg) between Least-Squares Planes^a

	por- phyrin	I	II	pyr- role-1	pyr- role-2	pyr- role-3	pyr- role-4
porphyrin	...	1.1	1.5	12.5	16.4	16.0	12.1
I	1.2	12.9	15.3	16.1	13.1
II	13.9	15.4	14.9	13.3
pyrrole-1	23.8	28.0	11.2
pyrrole-2	22.8	28.2
pyrrole-3	22.3

^a See Table IX for definition of planes.

While the porphyrin skeleton shows a marked ruffling, this has little effect on the coordination environment of the copper(II) ion. The four N_p atoms are coplanar within experimental error (Table IX) and the Cu ion lies within this plane. The four N_p least-

squares plane and the 24-atom porphyrinato least-squares plane do not coincide. The former is displaced about 0.04 \AA from the latter toward the exterior of the dimer structure.

Conclusions

The X-ray structural analysis of $\text{Cu}_2(\text{FTF } 6-3,2\text{-NH diamide}) \cdot 2\text{H}_2\text{O} \cdot \text{C}_7\text{H}_8$ confirms the formulation of FTF 6-3,2-NH diamide 17 and by implication that presumed for the other "face to face" porphyrins. While some stereochemical features such as a ruffled porphyrinato core are not unexpected, the offset or shear displacement of the porphyrinato rings is a surprise. The peculiar conformation of the amide linkage permitting the displacement and close approach of the porphyrin rings is equally surprising; the flexibility of the interporphyrin linkages even with the constraint of a planar amide group was underestimated. To

ensure the close and truly "face to face" approach of two metalloporphyrins, it appears that the shortest linkages and/or linkages with the fewest degrees of freedom are desired. Thus FTF 7 and FTF 6 systems appear unsatisfactory for this purpose (except note FTF 7-2,2-NH diurea which, although it probably puts metals too far apart, exhibits a sharp room temperature NMR spectrum perhaps because the urea linkage is so conformationally restricted as to permit only simple, relatively unrestrained intramolecular motions). Attention should be focused on FTF 5 and FTF 4 systems which possess linkages with little conformational freedom.

It is interesting that the intramolecular flexibility of motion, which was speculated² to be of importance in the accommodation of and chemical transformation of small molecules within the "face to face" porphyrin cavity, may not be so desirable after all. The factors which influence the stereochemistry of the dimer system are more complex than first realized, as illustrated by the peculiar structure of Cu₂(FTF 6-3,2-NH diamide). Shorter, more rigid linkages appear necessary if the desired interactions with small molecules are to be achieved.

Experimental Section

Reagents and Solvents. All solvents and reagents were of commercial, reagent grade quality and were used without further purification except as noted. Benzene (thiophene free), THF, and pyridine were refluxed with and distilled from CaH₂ under N₂. Toluene was distilled under N₂ from Na. DMF was distilled under reduced pressure from BaO onto Linde 4A molecular sieves. Ethanol-free CHCl₃ was obtained by washing with H₂O, drying over MgSO₄, and distilling. Hexane was stirred with concentrated H₂SO₄ for 12–24 h and then with 0.1 M KMnO₄ in 1 M H₂SO₄ for 12 h, washed with H₂O, dried over MgSO₄, and distilled. Benzyl alcohol was used from newly opened bottles or else freshly distilled under reduced pressure. Triethylamine was refluxed with and then distilled from phthalic anhydride and then from sodium under N₂. Methanesulfonyl chloride, oxalyl chloride, and CH(OMe)₃ were distilled before use. Thionyl chloride was refluxed with and distilled from triphenyl phosphite. Trichloroacetic acid was dried by azeotropic distillation and crystallization from a benzene solution. The benzene was removed in vacuo, and the dry Cl₃CCO₂H (hygroscopic) was dissolved in CH₂Cl₂, avoiding exposure to atmospheric moisture.

For column chromatography, the silica gel was W. R. Grace type 62 (60–200 mesh) and the alumina was Woelm neutral alumina (activity I). Alumina of activity III was prepared by adding H₂O to the activity I alumina. For TLC, Analtech, Inc., silica and alumina plates were used.

Physical and Spectroscopic Methods. Melting points were obtained on a Mel-temp Laboratory Devices capillary apparatus and are uncorrected. Electronic spectra were obtained on a Beckman DB-G or Cary 219 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 457 or Beckman Acculab 3 spectrometer. A Varian Instruments T-60 or Varian XL-100 were used for ¹H NMR spectra. Pulsed Fourier transform spectra were obtained on the XL-100 instrument using a Nicolet Technology Corporation Model 1180 FT disk data system. All ¹H NMR spectra of the "face to face" dimers were recorded from samples at 90 °C dissolved in C₂D₂Cl₄. Temperature calibration (to ±2 °C) was achieved by monitoring the chemical shift difference between the hydroxyl and methylene protons of ethylene glycol. Mass spectra were obtained on a Varian Instruments MAT 44 GC-MS system using the direct insertion mode, 70-eV ionization energy, and temperatures of 200–250 °C for porphyrin monomers. Dimers required temperatures of 300–350 °C to generate detectable molecular ion peaks. Field desorption mass spectra were obtained on a Varian/MAT 731 mass spectrometer. Solution molecular weights were determined on a Hitachi Perkin-Elmer Model 115 apparatus. Elemental analyses were performed by the Stanford Microanalytical Laboratory.

Some of the free-base porphyrins (the diamino and "face to face" porphyrins in particular) were found to be very sensitive to light and/or oxygen, especially when dispersed on chromatographic plates or columns or in dilute solution. These compounds were manipulated in subdued light (no fluorescent illumination) and chromatographed in the dark (columns were wrapped in aluminum foil).

Synthesis of 5,15-Dialkyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrins. Ethyl 3-ethyl-5-iodo-4-methylpyrrole-2-carboxylate. A mixture of NaHCO₃ (150 g, 1.8 mol), H₂O (600 mL), and 1,2-dichloroethane (700 mL) was heated to 50 °C and then, with vigorous mechanical stirring, 2-(carboethoxy)-3-ethyl-4-methylpyrrole-5-carboxylic acid⁹ (119 g, 0.53 mol) was added slowly. A solution of iodine (150 g, 0.595 mol) and NaI (190 g, 1.27 mol) in H₂O (600 mL) was added over 5 min, and the resulting mixture was heated at reflux for 1

h. After the mixture was cooled, sodium thiosulfate (ca. 20 g) was added to discharge the excess iodine. The organic phase was then separated, and the aqueous phase was extracted with 3 × 150 mL of CHCl₃. The combined organic extracts were washed with 4 × 200 mL of H₂O, dried over Na₂SO₄, and filtered. Removal of solvent left an off-white solid which was crystallized from hot hexane to give white needles (149.7 g, 0.487 mol). The filtrate afforded a usable second crop (4.94 g): total yield 95%; mp 120–121 °C. Anal. Calcd for C₁₀H₁₄INO₂: C, 39.10; H, 4.59; N, 4.56; I, 41.32. Found: C, 39.01; H, 4.64; N, 4.58; I, 41.20.

Ethyl 3-Ethyl-4-methylpyrrole-2-carboxylate. Ethyl 3-ethyl-5-iodo-4-methylpyrrole-2-carboxylate (40 g, 0.13 mol) in boiling EtOH (250 mL) was treated with a solution of sodium iodide (31.13 g, 0.21 mol) in H₂O (250 mL), followed by concentrated HCl (16.3 mL). Iodine was rapidly formed. After 10–15 min a solution of NaHSO₃ (20.8 g, 0.2 mol) in H₂O (30 mL) was added and the mixture was diluted with H₂O and extracted with CH₂Cl₂. The CH₂Cl₂ extracts were washed with 10% NaHCO₃ and H₂O, dried, filtered, and evaporated to a residue which was crystallized from hexane to give pale yellow prisms (18.8 g, 80%), mp 72–75 °C (lit.⁹ 75 °C). NMR (CDCl₃): δ 1.1 (t, 3, CH₂CH₃), 1.33 (t, 3, OCH₂CH₃), 2.0 (s, 3, CH₃), 2.73 (q, 2, CH₂CH₃), 4.27 (q, 2, OCH₂CH₃), 6.55 (d, 1, α-H), 8.7 (s (br), 1, NH).

Benzyl 3-Ethyl-4-methylpyrrole-2-carboxylate⁸ (2). This was prepared from the ethyl ester by the base-catalyzed transesterification method of Badger et al.³⁰ From the ethyl ester (61.1 g, 0.34 mol), the benzyl ester was crystallized from an equal volume of hexane to give 68.9 g. A second crop, 9.3 g, was obtained: total yield 78.2 g, 0.32 mol, 95%. NMR (CDCl₃): δ 1.12 (t, 3, CH₂CH₃), 2.03 (s, 3, CH₃), 2.8 (q, 2, CH₂CH₃), 5.32 (s, 2, OCH₂Ph), 6.65 (d, 1, α-H), 7.3–7.5 (m, 5, OCH₂Ph), 8.88 (s (br), 1, NH).

Ethyl 4,4-Dimethoxybutyrate (3a). Ethyl 4-pentenoate¹¹ (5 g, 39 mmol) in MeOH (100 mL) was treated with ozone at <–70 °C from a Wellsbach generator until the blue color persisted (ca. 50 min). The excess ozone was removed by passing oxygen through the mixture, while maintaining the temperature <–70 °C. Dimethyl sulfide (5 mL) was then added and the mixture allowed to warm slowly to room temperature overnight. A starch iodide test for oxidants was negative. The MeOH was then removed at <40 °C. (All glassware coming in contact with the product was rinsed with dilute NH₄OH prior to use.) The colorless oily residue was dissolved in CHCl₃ (100 mL) and washed twice with H₂O. The H₂O washes were back-extracted with CHCl₃, and the organic extracts were dried over K₂CO₃, filtered, and concentrated to a colorless oil, the acetal ester (6.19 g, 90%), which was characterized by NMR spectroscopy and used without further manipulation for dipyrromethane preparations. Attempts to distill the product have led to decomposition. NMR (CDCl₃): δ 1.27 (t, 3, OCH₂CH₃), 1.7–2.8 (m, 4, CH₂CH₃), 3.33 (s, 6, OCH₃), 4.15 (q, 2, OCH₂CH₃), 4.41 (t, 1, O–CH–O); no CHO.

Ethyl 3,3-Diethoxypropionate (3b). Freshly cut potassium (400 mg) was carefully added to absolute EtOH (90 mL) under N₂, and to this a solution of ethyl propionate (20 g, 0.204 mol) in absolute EtOH (20 mL) was added slowly (the reaction is very exothermic). The solution (pale yellow) was stirred for 12 h under N₂, and then poured directly into 600 mL of H₂O. The H₂O layer was extracted with 3 × 200 mL of Et₂O. The H₂O layer was saturated with NaCl and reextracted with a further 3 × 200 mL of Et₂O. The combined organic extracts were washed with 200 mL of 5% NaHCO₃ and then 200 mL of H₂O, dried over K₂CO₃, and filtered. Slow and thorough removal of Et₂O at reduced pressure yielded 38.6 g, 0.203 mol, 100%, of the acetal as a colorless oil, the purity of which was checked by NMR means prior to use. NMR (CDCl₃): δ 1.17 (t, 6, OCH₂CH₃), 1.23 (t, 3, (O)COCH₂CH₃), 2.62 (d, 2, CH₂), 3.5–3.9 (m, 4, OCH₂CH₃), 4.15 (q, 2, (O)COCH₂CH₃), 4.93 (t, 1, O–CH–O). IR (film): ν(CO) 1735 cm^{–1}.

Ethyl 4,4-Bis(5-((benzyloxy)carbonyl)-4-ethyl-3-methylpyrrol-2-yl)-butyrate (4a). Benzyl 3-ethyl-4-methylpyrrole-2-carboxylate (2) (10 g, 41 mmol) was dissolved in dry benzene (125 mL), and *p*-toluenesulfonic acid (150 mg) was added. The solution was brought to reflux under N₂ and ethyl 4,4-dimethoxybutyrate (3a) (4.35 g, 25 mmol) was added. After 2.5 h of reflux the mixture was cooled, washed with 2 × 50 mL of 5% Na₂CO₃ and 2 × 50 mL of H₂O, dried over MgSO₄, and filtered. The filtrate was evaporated at reduced pressure to a yellow-brown oil which was crystallized from EtOH (50 mL) to give yellowish crystals of the dipyrromethane (8.3 g, 67%). For analysis, the product was recrystallized from EtOH; mp 138.5–139 °C. NMR (CDCl₃): δ 0.9–1.4 (m, 9, CH₂CH₃ + OCH₂CH₃), 2.0 (s, 6, CH₃), 2.2–2.5 (m, 4, (O)CCH₂CH₂), 2.73 (q, 4, CH₂CH₃), 4.08 (q, 2, OCH₂CH₃), 4.28 (t, 1, methine-H), 5.23 (s, 4, OCH₂Ph), 7.2–7.4 (m, 10, OCH₂Ph). Anal. Calcd for C₃₆H₄₂N₂O₆: C, 72.22; H, 7.07; N, 4.68. Found: C, 71.77; H, 6.84; N, 4.53.

(30) Badger, G. M.; Jones, R. A.; Laslett, R. L. *Aust. J. Chem.* **1964**, *17*, 1157–1163.

Ethyl 3,3-Bis(5-((benzyloxy)carbonyl)-4-ethyl-3-methylpyrrol-2-yl)-propionate (4b). Benzyl 3-ethyl-4-methylpyrrole-2-carboxylate (**2**) (10.9 g, 42.3 mmol) was dissolved in dry benzene (100 mL), and *p*-toluenesulfonic acid (200 mg) was added. The solution was brought to reflux under N₂ and then ethyl 3,3-diethoxypropionate (**3b**) (14.5 g, 76 mmol) was added. After 24 h at reflux, or whenever the starting pyrrole had been consumed, the solution was cooled, washed with 2 × 100 mL of 10% Na₂CO₃ and then 2 × 100 mL of H₂O, dried over Na₂SO₄, and filtered. The filtrate was concentrated to a viscous oil which was crystallized from EtOH (50 mL). The crude product was recrystallized from CH₂Cl₂-hexane to give the dipyrromethane **4b** (8.9 g, 15.1 mmol, 72%), mp 116–118 °C. NMR (CDCl₃): δ 1.03 (2t, 9, CH₂CH₃ + OCH₂CH₃), 2.0 (s, 6, CH₃), 2.72 (q, 4, CH₂CH₃), 3.13 (d, 2, (O)CCH₂CH₃), 4.0 (q, 2, OCH₂CH₃), 4.8 (t, 1, methine-H), 5.25 (s, 4, OCH₂Ph), 7.2–7.5 (m, 10, OCH₂Ph), 10.03 (s, 2, NH). Anal. Calcd for C₃₃H₄₀N₂O₆: C, 71.89; H, 6.90; N, 4.79. Found: C, 71.76; H, 6.68; N, 4.82.

Ethyl Bis(5-((benzyloxy)carbonyl)-4-ethyl-3-methylpyrrol-2-yl)acetate (4c). Benzyl 3-ethyl-4-methylpyrrole-2-carboxylate (**2**) (3.0 g, 12.3 mmol) was dissolved in dry benzene (50 mL), and *p*-toluenesulfonic acid (50 mg) was added. The solution was brought to reflux under N₂, and ethyl diethoxyacetate (**3c**) (3.26 g, 18.5 mmol) was added. The solution was heated at reflux for 24 h under N₂. After the usual workup the product was crystallized from ethanol (50 mL) to give pale brown crystals (2.83 g, 80%). The crude product was recrystallized from ethanol (2.70 g, 4.73 mmol, 77%); mp 124.5–126.5 °C. NMR (CDCl₃): δ 1.07 (t, 6, CH₂CH₃), 1.23 (t, 3, OCH₂CH₃), 1.9 (s, 6, CH₃), 2.73 (q, 4, CH₂CH₃), 4.18 (q, 2, OCH₂CH₃), 5.07 (s, 1, methine-H), 5.27 (s, 4, OCH₂Ph), 7.2–7.5 (m, 10, OCH₂Ph), 9.1 (s (br), 2, NH). Anal. Calcd for C₃₄H₃₈N₂O₆: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.84; H, 6.82; N, 4.85.

Ethyl 4,4-Bis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)butyrate (5a). The dipyrromethane dibenzyl ester **4a** (11.3 g, 18.9 mmol) was hydrogenolyzed in the same manner to hydrogenolyze the ethyl propionate analogue **4b** (vide infra) using 10% Pd on C (350 mg), 7 drops of Et₃N, and THF (300 mL). Uptake was complete (850 mL) in 3 h, and the solution was filtered and reduced in volume at 40 °C to give a gummy white residue. Trituration with pentane produced a powdery white solid, the dipyrromethane dicarboxylic acid (8.12 g, 18.4 mmol, 97%). This was used for porphyrin preparations without further purification. NMR (CDCl₃-CD₃C(O)CD₃): δ 0.9–1.4 (m, 9, CH₂CH₃ + OCH₂CH₃), 2.07 (s, 6, CH₃), 2.2–2.5 (m, 4, (O)CCH₂CH₃), 2.75 (q, 4, CH₂CH₃), 4.05 (q, 2, OCH₂CH₃), 4.42 (t, 1, methine-H), 8.5 (s (br), 2, NH), 11.12 (s (br), 2, CO₂H); no benzyl groups.

Ethyl 3,3-Bis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)propionate (5b). The dipyrromethane dibenzyl ester **4b** (11.1 g, 0.019 mol) was dissolved in THF (250 mL). On an atmospheric hydrogenation manifold 10% Pd on C (200 mg) and 4 drops of Et₃N were equilibrated in 20 mL of THF for about 15 min. The dipyrromethane solution was then added and hydrogenolysis proceeded to completion (900 mL) in about 3 h. The mixture was filtered through Celite which was thoroughly washed with THF. The filtrate was concentrated at reduced pressure (40 °C) to a milk white paste to which hexane (200 mL) was added. Trituration and scratching produced a powdery white solid which was filtered and dried at ambient temperature in vacuo. This dipyrromethane dicarboxylic acid (7.7 g, 0.019 mol, 100%) was used for porphyrin preparations without further purification. NMR (CDCl₃-CD₃C(O)CD₃): δ 1.08 (m, 9, CH₂CH₃ + OCH₂CH₃), 2.1 (s, 6, CH₃), 2.75 (q, 4, CH₂CH₃), 3.13 (d, 2, (O)CCH₂CH₃), 4.0 (q, 2, OCH₂CH₃), 4.83 (t, 1, methine-H), 8.28 (s (br), 2, NH), 11.08 (s (br), 2, CO₂H); no benzyl groups.

Ethyl Bis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)acetate (5c). The dipyrromethane dibenzyl ester **4c** (2.70 g, 4.73 mmol) was hydrogenolyzed in the same manner as the ethyl propionate analogue **3b** by using 10% Pd on C (100 mg), 3 drops of Et₃N, and THF (100 mL). After uptake was complete (205 mL) in 1.5 h, the solution was filtered and concentrated to 3–5 mL (<40 °C), and hexane (200 mL) was added. Trituration produced a white powdery precipitate, the dipyrromethane dicarboxylic acid (1.86 g, 4.7 mmol, 100%). This product was used for porphyrin preparations without further purification.

5,15-Bis(2-(ethoxycarbonyl)ethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (6a) (C3 Diester Porphyrin). The dipyrromethane dicarboxylic acid **5a** (5 g, 12 mmol) was slurried in reagent grade CH₂Cl₂ (1.0 L), dry Cl₃CCO₂H (22.7 g, 0.14 mol) was added, followed by distilled CH(OMe)₃ (10.5 g, 0.1 mol), and the mixture was heated at reflux, while being protected from light and moisture, for 24 h after which time *p*-benzoquinone (1.3 g) was added and reflux continued for 2 h. The mixture was then cooled, washed with 2 × 500 mL of 10% Na₂CO₃ and then 2 × 200 mL of H₂O, dried over K₂CO₃, filtered, and concentrated at reduced pressure to 200 mL. Ethanol (200 mL) was added, and continued slow evaporation gave red-violet crystals of the porphyrin (1.75 g, 43%) from about 150 mL. The crystals were filtered and washed with

EtOH until the washings were colorless. For analysis, the product was crystallized by the vapor diffusion of pentane into a CHCl₃ solution. The crude product is of satisfactory purity for subsequent reactions; mp 253–255 °C (sintering). IR (KBr): ν(CO) 1725 cm⁻¹. NMR (CDCl₃): δ 1.32 (t, 6, OCH₂CH₃), 1.85 (t, 12, CH₂CH₃), 3.1 (m, 4, C(O)-CH₂CH₂), 3.63 (s, 12, CH₃), 4.1 (q, 8, CH₂CH₃), 4.32 (q, 4, OCH₂CH₃), 5.48 (m, 4, C(O)CH₂CH₂), 10.1 (s, 2, meso-H), -1.8 (s (br), 2, NH). Mass spectrum (70 eV): *m/e* 678, M⁺. Anal. Calcd for C₄₂H₅₄N₄O₄: C, 74.30; H, 8.02; N, 8.25. Found: C, 74.24; H, 8.04; N, 8.23. Mol wt (isopiestic): calcd, 679; found, 665.

5,15-Bis(2-(ethoxycarbonyl)methyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (6b) (C2 Diester Porphyrin). The dipyrromethane diacid **5b** (16.2 g, 40 mmol) was slurried in reagent grade CH₂Cl₂ (3.05 L), a solution of dry Cl₃CCO₂H in CH₂Cl₂ (92 mL, 5.2 M) was added, and to the resulting homogeneous solution was added redistilled CH(OMe)₃ (34 mL, 33 g, 0.32 mol). The solution was set to reflux protected by a drying tube. After 18 h at reflux, the mixture was oxidized by *p*-benzoquinone (4.3 g, 40 mmol) and reflux continued for 1.5 h. The mixture was cooled and reduced to about 1200 mL. The solution was neutralized by washing with 2 × 300 mL of 20% NaHCO₃, washed with 2 × 300 mL of H₂O, dried over K₂CO₃, and filtered, and the filtrate was concentrated to about 200 mL, whereupon 95% EtOH (500 mL) was added, and the volume was again slowly reduced to about 350 mL. The porphyrin crystallized from the EtOH. It was filtered and washed with EtOH until the washings were colorless. The product (6.75 g, 10.6 mmol, 52%) was pure on the basis of TLC and NMR analysis and was used for subsequent reactions without further purification. It was recrystallized from CH₂Cl₂-EtOH mixtures for analysis; mp 274–278 °C (sintering). IR (KBr): ν(CO) 1730 cm⁻¹. NMR (CDCl₃): δ 1.27 (t, 6, OCH₂CH₃), 1.8 (t, 12, CH₂CH₃), 3.4 (s, 12, CH₃), 4.05 (q, 8, CH₂CH₃), 4.37 (q, 4, OCH₂CH₃), 5.9 (s, 4, CH₂C(O)), 10.12 (s, 2, meso-H), -2.03 (s (br), 2, NH). Mass spectrum (70 eV): *m/e* 650, M⁺. Anal. Calcd for C₄₀H₅₀N₄O₄: C, 73.81; H, 7.74; N, 8.61. Found: C, 73.72; H, 7.72; N, 8.59.

5,15-Bis(2-(ethoxycarbonyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (6c) (C1 Diester Porphyrin). In a manner similar to the preparation of the porphyrin with the acetic acid side chain **6b**, the dipyrromethane diacid **5c** (1.6 g, 4.1 mmol) was slurried with CH₂Cl₂ (300 mL), a solution of Cl₃CCO₂H in CH₂Cl₂ was added (8 mL, 5.7 M), CH(OMe)₃ was added (3.2 mL, 3.2 g, 30 mmol), and the pink mixture was set to reflux for 18 h, open to the atmosphere. The UV/vis spectrum then revealed a strong Soret band at 400 nm which did not change after treatment with *p*-benzoquinone. Nevertheless, the quinone (500 mg) was added and heating continued for 1 h to ensure complete oxidation. The usual workup and crystallization methods produced small lustrous crystals (430 mg, 34%) of the porphyrin, which were filtered and washed with EtOH. IR (KBr): ν(CO) 1725 cm⁻¹. NMR (CDCl₃): δ 1.67 (t, 6, -OCH₂CH₃), 1.83 (t, 12, -CH₂CH₃), 3.38 (s, 12, -CH₃), 4.1 (q, 8, -CH₂CH₃), 5.03 (q, 4, -OCH₂CH₃), -2.92 (s (br), 2, NH). Mass spectrum (70 eV): *m/e* 622, M⁺. Anal. Calcd for C₃₈H₄₆N₄O₄: C, 73.28; H, 7.45; N, 9.00. Found: C, 72.91; H, 7.40; N, 8.79.

5,15-Bis(3-(hydroxypropyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (7a) (C3 Diol Porphyrin). The diester porphyrin **6a** (425 mg, 0.626 mmol) was dissolved in hot, dry THF (90 mL), and this cooled solution was added a few milliliters at a time to a stirred suspension of LiAlH₄ (0.215 g, 5.66 mmol) in THF (20 mL) under N₂. A red precipitate formed almost immediately, and the mixture was stirred for 1 h. The progress of the reaction was followed by TLC and if incomplete after 1 h, more LiAlH₄ was added until completion. The mixture was then cooled (ice bath), and H₂O (0.22 mL), 10% NaOH (0.22 mL), and 3 × 0.22 mL of H₂O were slowly and carefully added in that order. The mixture was extracted with CHCl₃ (300 mL) and then 200 mL. The combined organic extracts were washed with H₂O (200 mL), dried over K₂CO₃, filtered, and evaporated to dryness. The red, crude porphyrin diol was dissolved in hot CHCl₃, an equal volume of hot MeOH was added, and the product was crystallized (seeding) overnight (300 mg, 0.5 mmol). Concentration of the mother liquors gave a second crop (27 mg) pure to TLC for a total yield of 88%. IR (KBr): no carbonyl. NMR (pyridine-*d*₅): δ 1.82 (t, 12, CH₂CH₃), 2.65 (m, 4, OCH₂CH₂CH₂), 3.71 (s, 12, CH₃), 4.12 (m, 12, CH₂CH₃ + HOCH₂CH₂), 5.42 (m, 4, OCH₂CH₂CH₂), 6.36 (t, 2, OH), 10.36 (s, 2, meso-H), -1.0 (s (br), 2, NH); some assignments based on D₂O exchange. Mass spectrum (70 eV): *m/e* 594, M⁺. Anal. Calcd for C₃₈H₅₀N₄O₂: C, 76.73; H, 8.47; N, 9.42. Found: C, 76.51; H, 8.53; N, 9.21.

5,15-Bis(3-(methanesulfonato)propyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8a) (C3 Dimesylate Porphyrin). The diol porphyrin **7a** (319 mg, 0.536 mmol) was dissolved in dry pyridine (60 mL) with mild heating. The solution was then cooled in an ice bath, distilled methanesulfonyl chloride (0.7 mL) was added, and the mixture was

stirred at 0 °C in the dark for 1.5 h. The mixture was poured into ice water (200 mL), and brine (2 mL) was added to help coagulate the porphyrin. The crude product was collected, washed with H₂O, and dried in vacuo at 25 °C to give 405 mg, 100%. The crude product can be crystallized from concentrated CHCl₃ solutions or from CHCl₃-MeOH mixtures. IR (KBr): ν (S(O)₂O) 1175, 1355 cm⁻¹. NMR (CDCl₃): δ 1.8 (t, 12, CH₂CH₃), 2.42 (m, 4, CH₂CH₂CH₂), 2.77 (s, 6, CH₃S(O)₂O), 3.58 (s, 12, CH₃), 4.07 (m, 12, CH₂CH₃ + CH₂O), 5.22 (m, 4, OCH₂CH₂CH₂), 10.07 (s, 2, meso-H).

5,15-Bis(3-(methylamino)propyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (9a) (C3 NMe Diamine Porphyrin). A Fischer-Porter bottle (500 mL) with a stainless steel head was charged with the dimesylate porphyrin **8a** (238 mg, 0.317 mmol) and THF (200 mL). Methylamine was bubbled through the solution for 15 min to saturate it. The bottle was sealed, the pressure was set to 4 psi from the methylamine cylinder, and the stirred mixture was heated at 70 °C overnight, while the contents were protected from light. The mixture was then cooled and filtered. The solvent was removed, and the residue was redissolved in 4:1 CHCl₃-MeOH. This solution was washed with 2 × 30 mL of 0.1 N NaOH and 2 × 50 mL of H₂O, dried over K₂CO₃, filtered, and evaporated to dryness. The residue was dissolved in a minimum of 19:1 CHCl₃-MeOH and purified by chromatography on a dry-packed silica gel column (60–200 mesh, 2.5 cm × 25 cm), eluting first with 19:1:0.05 CHCl₃-MeOH-Et₃N to remove a faster moving impurity and then with 9:1:0.05 CHCl₃-MeOH-Et₃N to remove the porphyrin diamine. The solvent was evaporated; the residue (pure to TLC) was dissolved in a minimum of 9:1 CHCl₃-MeOH and crystallized by vapor diffusion in an atmosphere of pentane. NMR (CF₃CO₂H): δ 1.47 (t, 12, CH₂CH₃), 3.12 (m, 10), 3.3 (s, 12, CH₃), 3.88 (m, 12), 5.1 (m, 4, NCH₂CH₂CH₂), 7.47 (m (br), 4, -NH₂⁺), -2.93 (s (br), 4, pyrrolic NH). Anal. Calcd for C₄₀H₅₆N₆: C, 77.37; H, 9.09; N, 13.54. Found: C, 76.99; H, 9.08; N, 13.25. Mass spectrum (70 eV): *m/e* 620, M⁺.

5,15-Bis(2-hydroxyethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (7b) (C2 Diol Porphyrin). The diester porphyrin **6b** (1.0 g, 1.54 mmol) was dissolved in warm, dry THF (600 mL) under N₂. LiAlH₄ (400 mg, 10.5 mmol) was added to the stirred solution, and the reaction was monitored by TLC until complete (5–10 min). The reaction was promptly quenched by the careful addition of H₂O, then mixed with more H₂O (600 mL), and extracted with CH₂Cl₂ (800 mL). The aqueous phase was extracted further with 2 × 300 mL of CH₂Cl₂, and the combined organic extracts were dried over K₂CO₃, filtered, and evaporated to a powdery solid. The solid was dried in vacuo for 1 h, whereupon 300 mL of EtOAc was added and the resulting slurry was filtered to leave a brick red solid. This material was washed with a little EtOAc and dried. The diol porphyrin (0.76 g, 1.34 mmol, 87%) was used without further purification for the preparation of the dimesylate. An analytically pure sample was obtained as deep reddish needles by the slow evaporation of a CH₂Cl₂-EtOH solution. IR (KBr): no carbonyl. NMR (CF₃CO₂H): δ 1.5 (t, 12, CH₂CH₃), 3.38 (s, 12, CH₃), 3.87 (q, 8, CH₂CH₃), 5.2–5.7 (m, 8, CH₂CH₂O), -3.0 (s (br), 4, NH). Anal. Calcd for C₃₆H₄₆N₄O₂: C, 76.29; H, 8.18; N, 9.89. Found: C, 75.87; H, 8.20; N, 9.64.

5,15-Bis(2-(methanesulfonato)ethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8b) (C2 Dimesylate Porphyrin). The diol porphyrin **7b** (0.304 g, 0.536 mmol) was dissolved in dry pyridine (100 mL), and the mixture was placed under N₂ and cooled to 0 °C. About 0.5 mL of distilled methanesulfonyl chloride was added, and the course of the reaction was monitored by TLC. When all the slower moving bands (presumed diol and mono-ol) had disappeared (15–45 min), the mixture was poured onto crushed ice (300 mL). The product was collected, washed with H₂O and MeOH, and dried by suction (380 mg, 0.525 mmol, 98%). It was used without further purification in displacement reactions. The powdered product could be crystallized from CH₂Cl₂-EtOH to give dark red needles. IR (KBr): ν (S(O)₂O) 1175, 1355 cm⁻¹. NMR (CDCl₃): δ 1.83 (t, 12, CH₂CH₃), 2.55 (s, 6, CH₃S(O)₂), 3.63 (s, 12, CH₃), 4.1 (q, 8, CH₂CH₃), 4.82 (m, 4, OCH₂CH₂), 5.62 (m, 4, OCH₂CH₂).

5,15-Bis(2-(methylamino)ethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (9b) (C2 NMe Diamine Porphyrin). A Carius tube (24 cm × 20 mm (internal diameter), 3 mm thick walls) was charged with the dimesylate porphyrin **8b** (400 mg, 0.553 mmol) and dry THF added to about one-third the volume of the tube. The contents of the tube were degassed twice, and methylamine was condensed into the tube (liquid N₂) until a volume of amine of about one-third the volume of the tube had been collected. The tube was then frozen, evacuated, and sealed. While the stirred contents were being protected from light, the tube was heated in an oil bath at 85 °C for 24 h. The tube was then frozen to liquid N₂ temperature and cracked open. Upon being warmed to room temperature, the contents of the tube were poured into CH₂Cl₂ (300 mL) and

the organic solution was then washed with 2 × 200 mL of H₂O and dried over K₂CO₃. The solvent was removed to leave a semicrystalline powdery solid which was dried in vacuo for several hours followed by the addition of EtOAc (300 mL). The solid was filtered and washed with EtOAc until the washings were colorless to leave a fluffy red-brown solid (306 mg, 93%), used as such for "face to face" porphyrin syntheses. NMR (CDCl₃): δ 1.4 (s (br), 2, amino-NH?), 1.8 (t, 12, CH₂CH₃), 2.5 (s, 6, NCH₃), 3.2 (m, 4, NCH₂), 3.6 (s, 12, CH₃), 4.1 (q, 8, CH₂CH₃), 5.27 (m, 4, NCH₂CH₂), -1.78 (s (br), 2, pyrrolic NH). Anal. Calcd for C₃₈H₅₂N₆: C, 76.98; H, 8.84; N, 14.18. Found: C, 76.61; H, 8.75; N, 13.72.

5,15-Bis(2-carboxyethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Dihydrochloride (10a) (C3 Diacid Porphyrin). The diester porphyrin **6a** (1 g, 1.47 mmol) was stirred in 6 N HCl (100 mL) for 10 h. The porphyrin initially dissolved and the resultant product crystallized from the reaction medium. The solid was filtered off, washed with dilute HCl (5 mL), and dried in vacuo to give 1.01 g (99%). It was used without further purification. The NMR spectrum revealed complete hydrolysis. NMR (CF₃CO₂H): δ 1.63 (t, 12, CH₂CH₃), 3.43 (s, 12, CH₃), 3.9 (m, 12, CH₂CH₃ + HO₂CCH₂), 5.5 (m, 4, HO₂CCH₂CH₂); ethyl ester, if present, displays a quartet from the ethoxy group at δ 4.55.

5,15-Bis(2-aminoethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (12a) (C2 Diamine Porphyrin). The dicarboxylic acid porphyrin dihydrochloride **10a** (500 mg, 0.72 mmol) was stirred in distilled oxalyl chloride (10 mL) for 4 h (the porphyrin dissolves during the first 2–3 h), and the oxalyl chloride was removed in vacuo. The residue, a blue-green powder, was dried in vacuo for an additional hour. To this residue were added CH₂Cl₂ (60 mL) and dry acetone (40 mL), and immediately with vigorous stirring a solution of NaN₃ (5.6 g) in H₂O (20 mL) was added. The mixture was stirred for 15 min and poured into CHCl₃ (250 mL). The organic layer was separated, washed with 5% NaHCO₃ and then H₂O, dried over Na₂SO₄, filtered, and evaporated to a volume of about 20 mL. Benzene (50 mL) was added and the solution evaporated to dryness (<35 °C). Dry benzene (200 mL) was added and the mixture heated at reflux for 2 h in the dark. A 6 N solution of HCl (80 mL) was added, and heating was continued for 1 h. The organic layer was separated from the cooled porphyrin-containing aqueous acid layer, and to this latter phase was added a mixture (300 mL) of 5:1 CHCl₃-MeOH. While the mixture was stirred very rapidly, solid Na₂CO₃ (40–50 g) was added slowly until the mixture was basic. The organic layer was separated, washed with H₂O, dried over K₂CO₃, filtered, and evaporated to give a residue of the crude diamino porphyrin.

These manipulations were repeated on another 500 mg of diacid porphyrin dihydrochloride **10a**, and the crude diamino porphyrin products were combined, dissolved in 19:1 CHCl₃-MeOH (125 mL), and loaded onto a dry-packed silica gel column (60–200 mesh, 5 cm × 30 cm). Elution with 19:1:0.05 CHCl₃-MeOH-Et₃N removed some faster moving impurities and then the major diamino porphyrin product in a form pure to TLC. Upon concentrating the solution and adding EtOAc, we obtained the porphyrin as a powder. Hexane was added to effect further precipitation. The powder was filtered off, washed with hexane and dried (500 mg, 61% from diacid). This crude product was suitable for "face to face" forming reactions. A sample for analysis was crystallized by vapor diffusion of pentane into a 9:1 CHCl₃-MeOH solution. NMR (CF₃CO₂H): δ 1.5 (t, 12, CH₂CH₃), 3.4 (s, 12, CH₃), 3.9 (q, 8, CH₂CH₃), 4.4 (m, 4, CH₂CH₂N⁺H₃), 5.62 (m, 4, CH₂CH₂N), 7.8 (s (br), 6, H₃N⁺), -2.73 (s (br), 4, pyrrolic NH). Mass spectrum (70 eV): *m/e* 564 M⁺. Anal. Calcd for C₃₆H₄₈N₆: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.64; H, 8.54; N, 14.87. An acetamide derivative revealed the presence of two acetamido groups in the NMR spectrum (CF₃CO₂H): δ 1.8 (s, 6, NHC(O)CH₃), 8.6 (s (br), 2, NHAc); no amine NH₃⁺ at δ 7.8.

5,15-Bis(carboxymethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Dihydrochloride (10b) (C2 Diacid Porphyrin). The diester porphyrin **6b** (1.0 g, 1.54 mmol) was added to a solution of 12 N HCl (35 mL) and CF₃CO₂H (5 mL), and the solution was stirred and heated at 80–85 °C for 16 h. The mixture (containing some precipitated diacid porphyrin) was cooled to room temperature, 12 N HCl (50 mL) added to precipitate completely the product, and the solid dicarboxylic acid filtered, washed with 3 × 20 mL of H₂O and then 2 × 10 mL of EtOH, and dried, giving 1.07 g, 1.53 mmol, 100%. NMR (CF₃CO₂H): δ 1.55 (t, 12, CH₂CH₃), 3.33 (s, 12, CH₃), 3.9 (q, 8, CH₂CH₃), 6.27 (s (br), 4, HO₂CH₂).

5,15-Bis((chlorocarbonyl)methyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin Dihydrochloride (11b) (C2 Diacid Chloride Porphyrin) and 5,15-Bis((azidocarbonyl)methyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (13b) (C2 Diacid Azide Porphyrin). The diacid porphyrin dihydrochloride **10b** (0.5 g, 0.79 mmol) was dissolved in CF₃CO₂H (10 mL) and the TFA was then removed in vacuo to leave a glossy gun-metal blue paste. This was dissolved in CH₂Cl₂ (20 mL)

which was then also removed in vacuo to leave a blue-green solid, which was dried in vacuo for an additional 15 min after which distilled oxalyl chloride (20 mL) was added. After 30 min the porphyrin had dissolved into the stirred solution. After 2 h the excess oxalyl chloride was removed in vacuo to leave a powdery solid which was dried in vacuo for 1 h before use. (The bis(acid chloride) porphyrin dihydrochloride **11b** prepared in this way was also used in the preparation of "face to face" porphyrins.)

The acid chloride so formed was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 °C in an ice bath, and, without delay, a solution of NaN_3 (1.5 g, 23 mmol) and tetra-*n*-butylammonium bromide (0.3 g, 1.4 mmol) in H_2O (10 mL) was added with vigorous stirring. A brick red precipitate formed quickly, and after 30 min this was filtered, washed with CH_2Cl_2 , H_2O , and EtOAc , and dried. The product bis(acid azide), 450 mg, 0.7 mmol, 88%, was used without further purification. IR (KBr): $\nu(\text{CO})$ 1710, $\nu(\text{N}_3)$ 2135 cm^{-1} .

5,15-Bis(isocyanatomethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (14b) (C1 Diisocyanate Porphyrin). The bis(acid azide) porphyrin **13b**, 450 mg, 0.7 mmol, was heated in dry benzene (30 mL) at reflux for 1 h. The solution was concentrated to about 20 mL and allowed to cool. The diisocyanate porphyrin crystallized as fluffy red needles (380 mg, 0.654 mmol, 92%). IR (KBr): $\nu(\text{NCO})$ 2240 cm^{-1} . Mass spectrum (70 eV): m/e 546, $\text{M}^+ - \text{NCO}$. Anal. Calcd for $\text{C}_{36}\text{H}_{40}\text{N}_6\text{O}_2$: C, 73.44; H, 6.85; N, 14.28. Found: C, 73.07; H, 6.66; N, 14.06.

5,15-Bis(aminomethyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (12b) (C1 Diamine Porphyrin). The diisocyanate porphyrin **14b** (472 mg, 0.8 mmol) was dissolved in dry benzene (300 mL) at reflux. A 6 N solution of HCl (200 mL) was added, and heating at reflux was continued for 1 h. The mixture was cooled and the organic layer separated and discarded. To the acid solution was added 9:1 CHCl_3 -MeOH (600 mL), and the mixture was cooled in an ice bath. While the two-phase system was stirred, 50% NaOH was added cautiously (the solvent may boil) until the mixture was fully neutralized. The organic layer, now containing the porphyrin, was washed with H_2O , dried over K_2CO_3 , and filtered, and toluene (100 mL) was added. The volume was reduced to about 50 mL, and the diaminoporphyrim was slowly crystallized upon standing. It was filtered, washed with toluene, and dried (326 mg, 0.61 mmol, 76%). For analysis it was recrystallized from hot toluene. NMR (CDCl_3): δ 1.83 (t, 12, CH_2CH_3), 3.67 (s, 12, CH_3), 4.08 (q, 8, CH_2CH_3), 6.10 (s, 4, CH_2N), 10.11 (s, 2, meso-H), -2.05 (s (br), 2, pyrrolic NH). Anal. Calcd for $\text{C}_{34}\text{H}_{44}\text{N}_6$: C, 76.08; H, 8.26; N, 15.66. Found: C, 75.45; H, 8.17; N, 15.16. Found: C, 76.09; H, 8.20; N, 15.03.

Syntheses of "Face to Face" Porphyrins. General Method for Diamide-Linked "Face to Face" Porphyrin Preparations. One "equivalent" of the appropriate bis(acid chloride) porphyrin was prepared as described in the preparation of acid azide porphyrins. The dicarboxylic acid porphyrin dihydrochloride was stirred with oxalyl chloride for 4 h. The solvent was removed in vacuo, and the residue dried in vacuo for 1 h. Residual traces of oxalyl chloride were then removed by passing dry CH_2Cl_2 vapor and N_2 through the flask for about 5 min. This crude bis(acid chloride) porphyrin dihydrochloride was dissolved under N_2 in dry CH_2Cl_2 and the solution loaded into a dry gas-tight syringe mounted on a motor-driven syringe pump (Sage Instruments Co., Model 355). A second, identical syringe was then filled with an equal volume of a solution of 1 equiv of the appropriate diamino porphyrin in warm dry CH_2Cl_2 or ethanol-free CHCl_3 , containing 0.5–1 mL of dry Et_3N to facilitate dissolution of the porphyrin. The contents of the two syringes were then simultaneously added, under an atmosphere of N_2 , to a three-necked creased sided flask (the syringes being attached via 1/16th in. diameter Teflon tubing and septa to the outer necks of the flask) containing rapidly stirred dichloromethane in sufficient quantity to ensure a final concentration of porphyrin reactants of 10^{-3} M. When the addition was completed (5–20 min), stirring was continued for 1 h. The mixture was then evaporated, and the residue was extracted with hot CHCl_3 . These extracts were filtered through a pad of Celite and the filtrate was washed with H_2O , dried over K_2CO_3 , and concentrated for preparative plate or column chromatography (if necessary) or else evaporated and the product crystallized directly from appropriate mixtures. The evaporation of CH_2Cl_2 -EtOH mixtures was a very convenient method. When successful, these reactions left virtually no unreacted diaminoporphyrim detectable by TLC.

FTF 7-3,3-NMe Diamide 15. This compound was prepared according to the general method by using the bis(acid chloride) porphyrin **11a**, derived from porphyrin diacid dihydrochloride **10a** (35 mg, 0.05 mmol) and the porphyrin diamine **9a** (31 mg, 0.05 mmol), each dissolved in CH_2Cl_2 (3.8 mL). The diamine solution contained Et_3N (0.25 mL). The reaction flask contained CH_2Cl_2 (40 mL). Addition time was 4 min. After the separation of insoluble materials the homogeneous mixture was chromatographically purified on a preparative silica gel plate (2000 μm), eluting with 99.5:0.5 CHCl_3 - Et_3N for 8 h. A faster moving brown band,

containing several uncharacterized components (UV/vis suggested they were monomeric porphyrin materials), preceded the purple-brown product which was isolated and crystallized as purple prisms by evaporating a CH_2Cl_2 -EtOH solution (26 mg, 43%). IR (CHCl_3 solution, Cu(II) complex): $\nu(\text{CO})$ 1630 cm^{-1} . Mol wt (isopiestic): calcd for $\text{C}_{78}\text{H}_{98}\text{N}_{10}\text{O}_2$, 1206; found, 1090. Mass spectrum (70 eV): m/e 602–607, M^{++} ; calcd 603. Anal. Calcd for $\text{C}_{78}\text{H}_{98}\text{N}_{10}\text{O}_2$: C, 77.57; H, 8.18; N, 11.60. Found: C, 76.96; H, 7.88; N, 11.45.

FTF 6-3,2-NMe Diamide 16. This compound was prepared according to the general method by using the bis(acid chloride) porphyrin **11a** (128 mg, 0.178 mmol) and the diamine porphyrin **9b** (105 mg, 0.178 mmol), each dissolved in CH_2Cl_2 (9.5 mL). The diamine solution contained Et_3N (0.5 mL). The reaction flask contained CH_2Cl_2 (200 mL), and the addition time was 10 min. After removing insoluble byproducts on Celite, the mixture was chromatographed in the same manner as the FTF 7-3,3-NMe diamide **15**. The dimer was crystallized from CH_2Cl_2 -EtOH by evaporation (100 mg, 48%). IR (KBr): $\nu(\text{CO})$ 1630 cm^{-1} . Mass spectrum (70 eV): m/e 1178–1184, M^+ ; calcd 1178. Anal. Calcd for $\text{C}_{76}\text{H}_{94}\text{N}_{10}\text{O}_2$: C, 77.38; H, 8.03; N, 11.88. Found: C, 77.20; H, 8.05; N, 11.83.

FTF 6-3,2-NH Diamide 17. This was prepared according to the general method by using the bis(acid chloride) porphyrin **11a** (40 mg, 0.057 mmol) and the diamine porphyrin **12a** (32 mg, 0.057 mmol), each dissolved in CH_2Cl_2 (5 mL). The diamine solution contained Et_3N (0.25 mL). The reaction flask contained CH_2Cl_2 (60 mL), and the addition time was 5 min. Workup and chromatographic purification was the same as for FTF 7-3,3-NMe diamide **15**. Crystallization from CH_2Cl_2 -EtOH gave 42 mg (64%) of porphyrin dimer as purple prisms. IR (CHCl_3 solution): $\nu(\text{CO})$ 1660 cm^{-1} . Mass spectrum (70 eV): m/e 1150–1154, M^+ ; calcd 1150. Anal. Calcd for $\text{C}_{74}\text{H}_{90}\text{N}_{10}\text{O}_2$: C, 77.18; H, 7.88; N, 12.16. Found: C, 76.61; H, 7.94; N, 12.05.

FTF 5-3,1-NH Diamide 18. This was prepared according to the general method by using the bis(acid chloride) porphyrin **11a** derived from porphyrin diacid dihydrochloride **10a** (200 mg, 0.286 mmol) and the porphyrin diamine **12b** (154 mg, 0.286 mmol). The acid chloride was dissolved in CH_2Cl_2 (20 mL). The diamine was dissolved in ethanol-free CHCl_3 (17 mL) containing Et_3N (3 mL). The reaction flask contained CH_2Cl_2 (300 mL), and the addition time was 20 min. After the removal of insoluble materials by passing the mixture through Celite, crystallization from CH_2Cl_2 -EtOH gave purple crystals (163 mg, 0.145 mmol, 51%). IR (CHCl_3 solution, Cu(II) complex): $\nu(\text{CO})$ 1660 cm^{-1} . NMR ($\text{Cl}_2\text{DCCDCl}_2$, 90 °C): δ 2.55 (m, 4, $\text{CH}_2\text{C}(\text{O})$), 3.81 (m, 16, β - CH_2CH_3), 5.24 (m, 4, $\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 6.41 (d, 4, CH_2NH). Mass spectrum (70 eV): m/e 1122–1128, M^+ ; calcd 1122. Anal. Calcd for $\text{C}_{72}\text{H}_{86}\text{N}_{10}\text{O}_2$: C, 76.97; H, 7.72; N, 12.47. Found: C, 77.09; H, 7.53; N, 12.42.

FTF 5-2,2-NMe Diamide 20. This compound was prepared according to the general method by using the bis(acid chloride) porphyrin **11b** derived from the diacid porphyrin dihydrochloride **10b** (200 mg, 0.3 mmol) and the diamine porphyrin **9b** (177 mg, 0.3 mmol), each dissolved in CH_2Cl_2 (10 mL). The diamine solution contained Et_3N (1.2 mL). The reaction flask contained CH_2Cl_2 (400 mL), and the addition time was 10 min. The mixture was evaporated to dryness, extracted with warm CHCl_3 , and passed through a plug of silica gel. The evaporated filtrate was dissolved in CH_2Cl_2 , washed with H_2O , dried over K_2CO_3 , filtered, and concentrated. Ethanol was added, and after a slow evaporation, purple crystals (88 mg, 25%) of the dimer formed. If desired, the product may be purified by preparative plate chromatography. IR (KBr): $\nu(\text{CO})$ 1620 cm^{-1} . Mass spectrum (70 eV): m/e 1152–1157, M^+ ; calcd 1150. Anal. Calcd for $\text{C}_{74}\text{H}_{90}\text{N}_{10}\text{O}_2$: C, 77.18; H, 7.88; N, 12.16. Found: C, 76.72; H, 7.81; N, 11.76.

FTF 4-2,1-NH Diamide 21. A preparation of this compound was attempted according to the general method by using the porphyrin bis(acid chloride) **11b** (40 mg, 0.06 mmol) and the porphyrin diamine **12b** (32 mg, 0.06 mmol). The acid chloride was dissolved in CH_2Cl_2 (10 mL) while the diamine was dissolved in ethanol-free CHCl_3 (9.5 mL) containing Et_3N (0.5 mL). The reaction flask contained CH_2Cl_2 (50 mL), and the addition time was 5 min. Considerable polymerization resulted and TLC indicated significant quantities of unreacted diamine porphyrin were present. Preparative TLC (2000 μm SiO_2 , 19:1 CHCl_3 -MeOH) of the washed and filtered CHCl_3 -soluble material gave a leading brown-purple band. This was collected and rechromatographed on a silica gel column (2.5 cm \times 25 cm, 60–200 mesh), eluting first with 99:1 CH_2Cl_2 - Et_2O to remove some faster moving material and then with 98:2 CH_2Cl_2 - Et_2O to remove the presumed porphyrin dimer (<2 mg, <3%). IR (CHCl_3 solution, Cu(II) complex): $\nu(\text{CO})$ 1640 cm^{-1} . A weak absorption at 1720 cm^{-1} suggested some impurity was present. Field desorption mass spectrum: m/e (recrystallized Cu(II) complex) 1216 \pm 1, M^+ ; calcd 1216.

FTF 6-3,2-NMe Diamine 22. The porphyrin dimer FTF 6-3,2-NMe diamide **16** (30 mg) was dissolved in dry THF (20 mL) under N_2 , and Red-al (200 μ L, Aldrich Chemical Co. brand of sodium bis(2-methoxyethoxy)dihydroaluminate in benzene, 3.5 M solution) was added. The reaction was monitored by TLC and observed to be complete within 45 min. The reaction was carefully quenched with H_2O , and the product was extracted into CH_2Cl_2 (100 mL). This extract was washed with H_2O (2×200 mL), dried over K_2CO_3 , filtered, and evaporated. The crude product was purified by preparative TLC (2000 μ m SiO_2 , 9:1:0.05 CH_2Cl_2 -MeOH- Et_3N), isolated, and crystallized by evaporating a 10-mL solution of 1:1 CH_2Cl_2 -EtOAc. Blue crystals (18 mg, 61%) were obtained. IR (KBr): no carbonyl. Mass spectrum (70 eV): m/e 1151–1157, M^+ ; calcd 1150. Anal. Calcd for $C_{76}H_{98}N_{10}$: C, 79.37; H, 8.57; N, 12.16. Found: C, 79.21; H, 8.22; N, 12.11.

FTF 7-2,2-NH Diurea 23. On one occasion, in the course of preparing a quantity of the diamine porphyrin **12a** by the hydrolysis of the corresponding diisocyanate in refluxing benzene/6 N HCl, a considerable amount of a much faster moving porphyrin product was isolated from the silica gel chromatography column used to purify large quantities (500–750 mg) of the porphyrin diamine. This product was further purified by preparative TLC (2000 μ m SiO_2 , $CHCl_3$ + 0.5% Et_3N) and crystallized from CH_2Cl_2 -EtOH by slow evaporation. It had the following characteristics which suggested that it may be a diurea-linked "face to face" dimer resulting from the combination of the porphyrin diamine **12a** with the corresponding diisocyanate before the hydrolysis of the latter could be completed. IR (KBr): $\nu(CO)$ 1650 cm^{-1} . NMR ($CDCl_3$): δ 1.43 (t, β - CH_2CH_3), 3.29 (s, β - CH_3), 3.68 (m, β - CH_2CH_3), 9.48 (s, meso-H), -2.44 (s, internal NH). Mass spectrum (70 eV): m/e 1179–1182, M^+ ; calcd 1180. Anal. Calcd for $C_{74}H_{92}N_{12}O_2$: C, 75.22; H, 7.85; N, 14.23. Found: C, 74.42; H, 7.73; N, 13.86. Treatment of this compound with acetic anhydride- Et_3N left it unchanged with respect to TLC, suggesting that no acylatable groups were present.

Syntheses of Hydrocarbon-Linked "Face to Face" Porphyrins. 1,1,8,8-Tetrakis(5-((benzyloxy)carbonyl)-4-ethyl-3-methylpyrrol-2-yl)-octane (24a). Ozone from a Wellsbach generator was passed through a solution of cyclooctene (4 mL) and methanol (150 mL) at $-70^\circ C$ until the blue color of O_3 persisted. The excess O_3 was swept out by O_2 , dimethyl sulfide (6 mL) added, and the mixture allowed to warm slowly to room temperature (overnight). A starch iodide test for oxidants was negative so the mixture was evaporated ($<50^\circ C$) to an oil which was dissolved in ether, washed with water, dried over K_2CO_3 , and evaporated to an oil (2 g). The 1H NMR spectrum showed this to be about 80% 1,8-octanedial with residual H_2O , MeOH, and Et_2O . It proved suitable for bis(dipyrromethane) preparations.

A mixture of benzyl 3-ethyl-4-methylpyrrole-2-carboxylate (**2**) (2.0 g), *p*-toluenesulfonic acid (100 mg), and benzene (150 mL) was brought to reflux under N_2 , and the crude 1,8-octanedial (1.1 mL) was added. During the course of 2 h more pyrrole (up to 3 g) was added until only the bis(dipyrromethane) was present (TLC). The cooled mixture was then washed with H_2O and $NaHCO_3$, dried over Na_2SO_4 , filtered, and evaporated to an oil. This was crystallized from 1:1 EtOH-hexane. For analysis the product was recrystallized from hot CH_2Cl_2 -hexane (4.1 g, 3.8 mmol, 74%); mp 105–107 $^\circ C$. NMR ($CDCl_3$): δ 0.84–1.28 (m, 20, CH_2CH_3 + $CHCH_2(CH_2)_4CH_2CH$), 1.9 (s (br), 16, CH_3 + $CHCH_2(CH_2)_4CH_2CH$), 2.68 (q, 8, CH_2CH_3), 4.02 (t, 2, $CH(CH_2)_6CH$), 5.18 (s, 8, OCH_2Ph), 7.31 (s (br), 20, OCH_2Ph). Anal. Calcd for $C_{68}H_{78}N_4O_8$: C, 75.67; H, 7.28; N, 5.19. Found: C, 75.94; H, 7.42; N, 5.09.

1,1,6,6-Tetrakis(5-((benzyloxy)carbonyl)-4-ethyl-3-methylpyrrol-2-yl)hexane (24b). Cyclohexene (5 mL) was treated with O_3 in MeOH (200 mL) at $-70^\circ C$, and the mixture was reductively worked up as in the case of cyclooctene above (8 mL of dimethyl sulfide was used). An oil was obtained as the crude product, the 1H NMR spectrum of which indicated it to be a ca. 4:1 mixture of dimethyl acetal and free aldehyde groups. This oil was used satisfactorily for bis(dipyrromethane) preparations.

In a manner similar to that used for the octane derivative above, a mixture of benzyl 3-ethyl-4-methylpyrrole-2-carboxylate (**2**) (3.0 g, 12.3 mmol), *p*-toluenesulfonic acid (100 mg), and benzene (100 mL) was brought to reflux under N_2 , and the crude 1,6-hexanedial (0.7 mL, 3.5 mmol) was added. After 3 h, 0.2 mL of dial was added to consume a residual amount of pyrrole and reflux continued for another 2 h. Workup of the mixture yielded an oil which solidified on trituration in EtOH (100 mL). This was recrystallized from hot CH_2Cl_2 -EtOH to give white microcrystals (2.1 g, 2.0 mmol, 65%); mp 200–202 $^\circ C$. NMR ($CDCl_3$): δ 1.03 (t (br), 16, CH_2CH_3 + $CHCH_2(CH_2)_2CH_2CH$), 1.85 (s (br), 16, CH_3 + $CHCH_2(CH_2)_2CH_2CH$), 2.68 (q, 8, CH_2CH_3), 3.97 (t, 2, methine-H), 5.25 (m, 8, OCH_2Ph), 7.25 (s (br), 20, OCH_2Ph). Anal. Calcd for $C_{66}H_{74}N_4O_8$: C, 75.40; H, 7.09; N, 5.33. Found: C, 75.25; H, 7.13; N, 5.15.

Table XI. Crystal Data and Data Collection Details for $Cu_2(FTF\ 6-3,2-NH\ diamide) \cdot 2H_2O \cdot C_7H_8$

formula	$Cu_2C_{74}N_{10}O_2H_{86} \cdot 2H_2O \cdot C_7H_8$ $Cu_2C_{81}H_{98}N_{10}O_4$
fw, amu	1402.82
space group	$C_{2h}^5-P2_1/c$
a, Å	11.878 (6)
b, Å	13.304 (7)
c, Å	23.725 (13)
β , deg	114.60 (2)
V, Å ³	3409
Z	2
ρ_{obsd} , ρ_{calcd} , g cm ⁻³	1.29 (1), 1.315 ^a
data collectn temp ^b	$-140^\circ C$
cryst shape, mm	faces of forms {100}, {001}, {102}, {011}; 0.31 \times 0.34 \times 0.56
cryst vol, mm ³	0.0420
radiatn, Å	graphite-monochromated Mo $K\alpha$, $\lambda(K\alpha_1) = 0.7093$
linear abs coeff, cm ⁻¹	6.83
transmissn factors	0.735–0.850
detector aperture	6.2 mm wide, 5.7 mm high, 32 cm from crystal
takeoff angle, deg	2.8
scan speed	2.0 $^\circ$ in 2 θ /min
scan range	1.0 $^\circ$ below $K\alpha_1$ to 1.0 $^\circ$ above $K\alpha_1$
bkgd counts	initially 10 s at each end of scan, then 20 s; with rescan option ^c
$\lambda^{-1} \sin \theta$, Å ⁻¹ , limits, deg	0.0431–0.5475, 3.5 $< 2\theta < 45.7^\circ$
data collected	$\pm h, k, l$
p	0.05
unique data	4663
unique data with $F_o^2 > 3\sigma(F_o^2)$	3213

^a Calculated by using the cell constants determined at room temperature from precession films ($a = 12.07$ Å, $b = 13.52$ Å, $c = 24.07$ Å, $\beta = 116.0^\circ$). ^b The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. ^c Lenhert, P. G. *J. App. Crystallogr.* 1975, 8, 568–570.

1,1,6,6-Tetrakis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)hexane. Hydrogenolysis was conducted as described for other dipyrromethanes. Using 10% Pd/C (100 mg), THF (300 mL), and 3 drops of Et_3N , we converted the corresponding benzyl tetraester **24b** (1.65 g, 1.57 mmol) to the tetraacid in 1 h (uptake 150 mL). After filtration through Celite the THF was evaporated to a volume of 20 mL and then hexane (300 mL) was added to precipitate the product (1.1 g, ca. 1.59 mmol, 100%) as a fine white powder. An NMR spectrum of this crude solid in TFA revealed no benzyl groups. It was used without further purification for a direct "face to face" porphyrin preparation.

1,1,8,8-Tetrakis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)octane. This was prepared from the benzyl tetraester **24a** in the same way that the hexane derivative was prepared.

FTF 6-C6 25a. This was prepared under the conditions used for the C2 diester porphyrin **6b**: from the bis(dipyrromethane) tetraacid (1.3 g, 1.9 mmol), dry Cl_3CCO_2H in CH_2Cl_2 (8.6 mL of a 5.2 M solution), $HC(OCH_3)_3$ (3 mL), and enough dry CH_2Cl_2 to bring the volume to 300 mL. After 18 h at reflux under N_2 , *p*-benzoquinone (600 mg) was added and reflux continued for 24 h. The mixture was worked up as described above and evaporated to a residue, insoluble in EtOH. To the dry residue was added EtOAc, dissolving most of the material. A small amount of crystalline material was filtered off and recrystallized from 1:1 $CHCl_3$ -EtOAc to give microcrystalline needles of the product (10 mg). Field desorption mass spectrum: m/e cluster at 1121, M^+ ; calcd 1120.

FTF 4-C4 25b. This porphyrin dimer was prepared by using conditions similar to those for the preparation of the C2 diester monomer porphyrin **6b**, using the bis(dipyrromethane) tetraacid (0.5 g, 0.73 mmol), dry Cl_3CCO_2H in CH_2Cl_2 (3.4 mL of 5.2 M solution), $HC(OMe)_3$ (1.3 mL), and enough CH_2Cl_2 to bring the volume to 120 mL. After being refluxed under N_2 for 18 h, the mixture was oxidized with *p*-benzoquinone (200 mg) and refluxing continued for another 2 h. The cooled mixture was diluted to 500 mL with CH_2Cl_2 , neutralized and washed in the usual way, dried (K_2CO_3), and evaporated to a minimal homogeneous volume. It was loaded onto a short silica gel (60–200 wash) dry-packed column (5-cm diameter \times 24-cm length). Elution with 9:1 CH_2Cl_2 -EtOAc produced 4 \times 250 mL fractions containing all of the

Table XII. Positional and Thermal Parameters for the Nongroup Atoms of $\text{Cu}_2(\text{FTF } 6-3,2\text{-NH diamide})\cdot 2\text{H}_2\text{O}\cdot\text{C}_7\text{H}_8$

ATOM	^A X	Y	Z	^B 011	022	033	012	013	023
Cu	0.014075(60)	0.051818(52)	0.132997(29)	33.46(72)	29.81(51)	5.29(17)	-3.34(48)	0.92(25)	1.25(24)
N(1)	-0.06190(39)	-0.07040(32)	0.08493(20)	32.8(41)	20.9(30)	10.5(11)	-0.7(28)	2.7(18)	2.8(15)
C(1)	-0.12775(49)	-0.08120(40)	0.02050(26)	30.2(51)	28.2(38)	12.0(15)	-2.2(35)	3.8(23)	-2.6(19)
C(2)	-0.15214(56)	-0.18871(42)	0.00646(33)	46.1(61)	18.1(37)	23.0(20)	-10.3(38)	9.8(28)	-7.4(22)
C(3)	-0.10745(58)	-0.23784(46)	0.06150(34)	57.6(66)	24.2(40)	25.8(21)	-0.8(42)	9.5(31)	3.7(24)
C(4)	-0.05222(54)	-0.16485(45)	0.10860(29)	45.9(59)	28.5(40)	16.6(17)	-5.2(40)	3.9(26)	4.9(22)
C(5)	0.01519(60)	-0.18896(48)	0.17155(34)	56.8(65)	39.0(45)	25.1(21)	8.9(44)	13.1(31)	26.1(25)
N(2)	0.11316(40)	-0.02759(36)	0.20871(20)	33.9(44)	47.7(38)	6.2(11)	1.9(32)	0.8(18)	6.7(16)
C(6)	0.09585(55)	-0.12815(49)	0.21656(29)	38.9(60)	51.2(48)	14.4(16)	17.7(43)	10.9(26)	16.1(24)
C(7)	0.18431(63)	-0.16158(63)	0.27660(30)	59.2(69)	98.3(67)	12.0(17)	41.6(59)	17.2(28)	20.6(29)
C(8)	0.25959(63)	-0.08375(62)	0.30299(28)	63.8(69)	100.0(69)	6.3(15)	54.7(57)	8.2(27)	11.8(25)
C(9)	0.21619(56)	0.00109(55)	0.26014(27)	42.1(60)	78.9(55)	6.0(14)	22.0(48)	5.1(25)	4.8(23)
C(10)	0.26456(55)	0.09894(59)	0.27032(26)	40.1(61)	87.6(60)	4.0(13)	-9.4(51)	-0.9(23)	-4.6(24)
N(3)	0.09098(42)	0.17438(37)	0.18173(21)	50.2(49)	39.3(36)	8.8(11)	-18.3(34)	7.9(20)	-7.6(17)
C(11)	0.19645(56)	0.18165(51)	0.23810(27)	53.8(63)	63.2(51)	7.1(14)	-35.2(47)	6.7(25)	-10.1(22)
C(12)	0.21335(69)	0.28604(57)	0.25672(32)	95.4(83)	72.6(58)	11.5(17)	-57.2(58)	16.3(32)	-19.1(26)
C(13)	0.12238(68)	0.33973(54)	0.21329(33)	98.4(82)	54.0(51)	17.9(19)	-38.5(54)	27.9(34)	-20.6(26)
C(14)	0.04994(58)	0.27016(48)	0.16503(29)	66.7(67)	37.7(45)	12.3(16)	-12.2(43)	15.2(28)	-10.7(21)
C(15)	-0.03912(59)	0.29788(44)	0.10712(31)	66.3(66)	25.2(39)	17.1(17)	-3.5(41)	12.0(29)	-6.2(22)
N(4)	-0.08344(40)	0.13266(32)	0.05771(20)	44.8(45)	17.2(29)	5.8(10)	-4.3(28)	4.9(18)	-0.4(13)
C(16)	-0.09433(53)	0.23538(41)	0.05674(28)	52.9(60)	18.3(36)	14.5(16)	-4.3(38)	12.8(26)	-0.2(19)
C(17)	-0.16297(58)	0.27157(46)	-0.00502(28)	69.2(67)	31.9(41)	12.0(16)	9.0(42)	8.8(27)	6.3(20)
C(18)	-0.19240(52)	0.18973(44)	-0.04264(26)	47.1(59)	35.4(41)	9.2(14)	12.8(38)	5.6(24)	6.8(20)
C(19)	-0.14702(50)	0.10212(41)	-0.00349(25)	38.1(54)	26.2(36)	8.5(14)	-1.2(36)	8.5(22)	2.1(18)
C(20)	-0.16445(48)	-0.00048(42)	-0.02103(25)	23.1(50)	31.0(37)	7.0(13)	-1.6(34)	0.3(21)	-2.8(19)
C(21)	-0.21311(67)	-0.24388(50)	-0.05426(36)	100.4(82)	40.1(47)	30.1(23)	-16.4(51)	29.6(37)	-18.1(28)
C(22)	-0.10558(75)	-0.35036(53)	0.07181(41)	116.1(93)	40.7(51)	38.2(28)	-17.3(57)	25.8(42)	4.9(31)
C(23)	-0.21225(88)	-0.38344(58)	0.08360(43)	213.1(14)	45.3(54)	45.9(32)	-10.8(69)	69.8(57)	-1.5(33)
C(24)	0.19518(67)	-0.26757(61)	0.30172(31)	102.9(84)	101.9(68)	17.3(18)	64.8(64)	27.3(34)	35.2(31)
C(25)	0.30862(66)	-0.32149(60)	0.30202(33)	87.7(79)	86.8(64)	17.8(19)	33.8(59)	12.3(32)	8.2(28)
C(26)	0.36340(72)	-0.08975(69)	0.36797(28)	122.9(94)	148.0(88)	4.9(14)	82.9(76)	0.5(30)	8.8(29)
C(27)	0.30431(84)	0.33180(68)	0.31652(34)	185.1(12)	112.6(77)	11.6(18)	-97.6(83)	14.2(39)	-17.8(31)
C(28)	0.09797(70)	0.45115(59)	0.20984(36)	118.4(88)	60.6(55)	28.0(22)	-34.6(61)	32.5(38)	-24.6(31)
C(29)	0.17216(74)	0.50500(53)	0.17992(38)	123.5(94)	43.1(48)	34.1(26)	-3.9(55)	34.3(42)	-7.4(29)
C(30)	-0.18772(72)	0.37973(52)	-0.02241(34)	116.9(91)	40.2(47)	21.2(20)	28.3(53)	12.7(35)	7.3(25)
C(31)	-0.31608(73)	0.41065(56)	-0.03181(33)	126.4(93)	65.8(57)	17.9(19)	28.9(60)	12.4(35)	4.0(27)
C(32)	-0.25828(67)	0.19990(54)	-0.11234(29)	111.6(82)	65.3(54)	9.2(15)	34.1(54)	11.4(30)	13.2(24)
C(33)	0.23178(49)	0.02428(44)	0.08982(25)	36.6(53)	48.0(44)	8.3(13)	-0.8(38)	4.1(22)	-10.1(19)
C(34)	0.37599(52)	0.03274(60)	0.11344(26)	32.5(55)	123.6(72)	5.3(13)	-28.4(53)	-2.7(22)	-19.2(26)
C(35)	0.4334(11)	0.00280(94)	0.18652(61)	34.1(11)	26.4(83)	9.4(32)	-3.3(75)	0.9(49)	-5.5(46)
O(1)	0.4658(14)	-0.08076(92)	0.21082(64)	70.1(11)	34.6(97)	11.6(34)	18.0(93)	-1.6(48)	5.7(40)
C-N	0.44908(49)	0.07332(54)	0.22148(27)	38.5(53)	95.8(63)	9.7(15)	-22.6(46)	4.8(23)	-10.4(26)
C(36)	0.48078(58)	0.10260(65)	0.28368(29)	36.1(61)	141.0(78)	8.3(15)	-7.4(56)	-2.9(25)	-18.4(28)
C(37)	0.40065(62)	0.11480(81)	0.31129(31)	48.0(68)	213.1(11)	9.5(16)	-24.2(70)	5.1(28)	-23.4(35)
O(1) #	0.4680(14)	-0.03825(93)	0.22875(65)	58.1(10)	31.1(10)	12.5(36)	22.5(87)	-3.8(49)	5.3(40)
N(5) #	0.41522(81)	0.10598(74)	0.17086(45)	26.7(88)	43.2(73)	10.5(26)	-0.2(63)	0.3(39)	9.9(35)
O	0.40397(43)	0.31742(34)	0.18588(22)	97.9(54)	54.9(35)	23.3(14)	-20.4(35)	14.1(23)	-18.2(18)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $\exp[-(\sigma_{11}^2 h^2 + \sigma_{22}^2 k^2 + \sigma_{33}^2 l^2 + 2\sigma_{12}hk + 2\sigma_{13}hl + 2\sigma_{23}kl)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

colored movable products. The latter 500 mL was evaporated to a powder which was suspended in a small amount of CH_2Cl_2 . EtOH (300 mL) was added, and after 30 min the microcrystalline product was filtered off and then recrystallized from hot CHCl_3 -EtOH to give small needles (10 mg). The first 500 mL of eluant contained no product. Mass

spectrum (70 eV): m/e 1066-1070, M^+ ; calcd 1068. Anal. Calcd for $\text{C}_{72}\text{H}_{88}\text{N}_8$: C, 81.16; H, 8.32; N, 10.52. Found: C, 79.73; H, 8.35; N, 10.06.

Introduction of Copper(II). Each copper(II) porphyrin was prepared in quantitative yield from the corresponding free-base porphyrin by

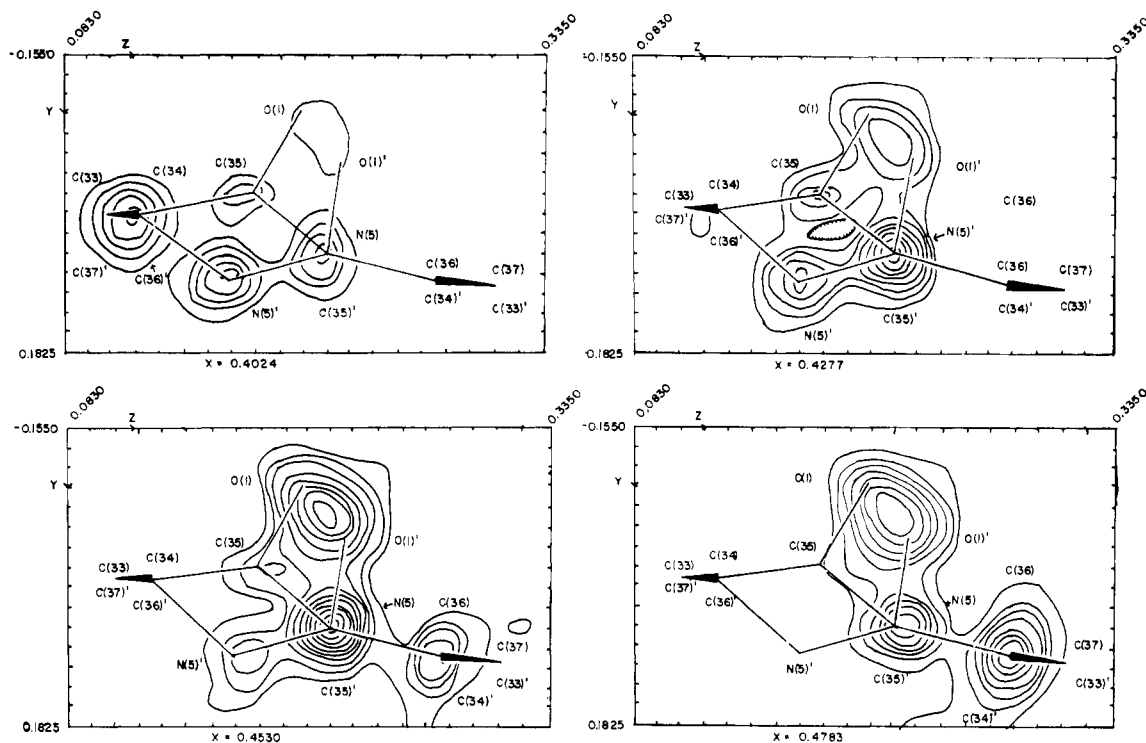


Figure 7. Sections of a difference Fourier map approximately parallel to the plane of the amide group and showing the disorder of the group. The interpretation of the electron density is indicated.

Table XIII. Derived Parameters for the Rigid Group Atoms of $\text{Cu}_2(\text{FTF 6-3,2-NH diamide}) \cdot 2\text{H}_2\text{O} \cdot \text{C}_7\text{H}_8$

ATOM	X	Y	Z	B, Å ²	ATOM	X	Y	Z	B, Å ²
SC(1)	0.49089(70)	-0.07301(32)	-0.00060(38)	3.12(26)	SC(5)	0.39715(78)	0.08981(48)	-0.03481(43)	4.44(33)
SC(2)	0.60293(63)	-0.02665(46)	0.03617(36)	1.64(21)	SC(6)	0.38800(63)	-0.01477(50)	-0.03609(38)	2.16(23)
SC(3)	0.61209(74)	0.07794(48)	0.03746(41)	3.39(27)	SC(7)	0.4809(11)	-0.0704(32)	-0.00200(56)	7.34(49)
SC(4)	0.50920(93)	0.13617(32)	0.00197(46)	4.43(32)					
RIGID GROUP PARAMETERS									
GROUP	X ^A	Y ^A	Z ^A	DELTA ^B	EPSILON	ETA			
SOLV	0.50004(64)	0.03158(32)	0.00068(34)	-0.0709(40)	3.1310(37)	0.2792(38)			

^A X, Y, AND Z ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^B THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIAN) HAVE BEEN DEFINED PREVIOUSLY: S.-J. LA PLACA AND J. A. IBERS, *ACTA CRYSTALLOGR.*, 18, 511 (1965).

adding copper acetate (saturated in MeOH) to a refluxing CHCl_3 solution of the porphyrin.³¹ The product was purified by chromatography on a short column of Woelm neutral alumina (activity III), eluting with CH_2Cl_2 in the case of porphyrin esters and amides.

X-ray Structure of the Cu(II) Complex of FTF 6-3,2-NH Diamide 17. Crystals of the Cu(II) derivative of FTF 6-3,2-NH diamide 17 were grown by permitting a toluene- CH_2Cl_2 solution to evaporate slowly in air. No precautions were taken to exclude moisture. On the basis of the structure determination the resultant crystals are $\text{Cu}_2(\text{FTF 6-3,2-NH diamide}) \cdot 2\text{H}_2\text{O} \cdot \text{C}_7\text{H}_8$. Preliminary precession and Weissenberg photographs of crystals of the complex displayed symmetry and systematic absences uniquely consistent with the monoclinic space group $C_{2h}^2-P2_1/c$. The dark red crystal selected for data collection upon a Picker FACS-I automatic diffractometer had acceptable mosaicity. Lattice parameters were obtained as previously described³² by hand-

centering 21 reflections in the range $0.2824 < \lambda^{-1} \sin \theta < 0.3784 \text{ \AA}^{-1}$ using $\text{Mo K}\alpha_1$ radiation ($\lambda = 0.70930$).

Important details of data collection are summarized in Table XI. The variation of six standard reflections, well-separated in reciprocal space, was monitored every 94 reflections. The variations were within counting statistics.

Solution and Refinement of the Structure. The usual procedures, computer programs, atomic scattering factors, and anomalous dispersion terms were used in the solution and refinement of the structure.³² In the initial stages the Northwestern University Vogelback Computing Center CDC6600 computer was used. Only those 3213 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. In the final cycles of anisotropic refinement the Lawrence Berkeley Laboratory CDC7600 computer was accessed by remote telephone connection and all data, including $F_o^2 < 0$, were used.

Coordinates for the copper atom were obtained from an unsharpened three-dimensional Patterson synthesis. The octaalkylporphyrinato skeleton and the meso substituents appeared in subsequent Fourier syntheses. A center of inversion is crystallographically imposed on the porphyrin dimer. Hence the two chains linking the two (porphyrinato)copper(II) groups suffer a statistical disorder since they lack an inherent center of symmetry. Consequently a close investigation was made to ascertain the nature of the disorder. The four carbon atoms α and β to the porphy-

(31) Fuhrhop, J.-H.; Smith, K. M. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 798.

(32) For example: Peng, S.-M.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8032-8036; Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273-3277.

rinato skeleton appeared as single though somewhat elongated peaks of electron density. Sections of the electron density map approximately in the plane of the amide group are presented in Figure 7 along with an interpretation. A region of electron density at hydrogen-bonding distance from the amide group was interpreted as a water molecule. Upon refinement the values for R and R_w on F dropped to 0.161 and 0.209. A somewhat ill-resolved region of electron density surrounding an inversion center was interpreted as a disordered toluene molecule. It was included in the model as a rigid group ($C-C = 1.392$ Å, $C-C-C = 120^\circ$, $C-CH_3 = 1.521$ Å) with individual isotropic thermal parameters; it behaved reasonably upon refinement. Group constraints on the pyrrole rings were released and the absorption correction applied (Gaussian integration on a $4 \times 4 \times 4$ grid). Most of the hydrogen atoms (except for some on the linking chain and those of the water molecule) were then located in difference Fourier syntheses and were included as a fixed contribution to F_c at their idealized positions ($C-H = 0.95$ Å, $C-C-H = 109.5^\circ$, $B_H = B_C + 1.0$ Å²). The final four cycles of refinement used all data; all atoms except the toluene solvate molecule were assigned anisotropic thermal parameters; the number of variable parameters was 438. At convergence the values for R and R_w on F^2 were 0.103 and 0.152. The standard error in an observation of unit weight was 1.48 e². For the portion of data having $F_o^2 > 3\sigma(F_o^2)$ the values for R and R_w on F were 0.063 and 0.073.

The minimized function was independent of the magnitude of F_o , but it did exhibit a not unexpected but slight dependence on the magnitude of $\lambda^{-1} \sin \theta$, with low-angle data returning a higher value. One atom in the linking chain has a grossly over-accentuated thermal ellipsoid. Removal of its contribution to F_c followed by a difference Fourier synthesis failed to reveal reasons for its anomalous shape. The highest peaks in

the final difference Fourier map, which was mostly flat and featureless, had heights 0.84 and 0.62 e Å⁻³ and were associated with the toluene solvate molecule.

Final nonhydrogen parameters are listed in Tables XII and XIII. Hydrogen atom parameters are given in Table XIV.²⁴ Table XV lists the values of $10|F_o|$ vs. $10|F_c|$.²⁴ A negative value indicates that $F_o^2 \leq 0$.

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Supplementary Material Available: Table IV, Selected Non-Bonded Intramolecular Contacts between Porphyrinato Planes; Table V, Non-Bonded Intermolecular Contacts (<3.75 Å); Table VI, Non-bonded Intermolecular Contacts (<2.80 Å and Involving Hydrogen Atoms); Table XIV, Hydrogen Atom Parameters; Table XV, Calculated and Observed Structure Amplitudes (21 pages). Ordering information is given on any current masthead page.

The Synthesis and X-ray Crystal Structure of a Novel Vilsmeier-Haack Adduct: [Tris(2-aminoethyl)amine][3-(dimethylamino)-2-aminoacrylyl chloride]cobalt(III) Chloride-Zinc Tetrachloride-Water¹

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Abstract: A dimethyliminium species, formed from dimethylformamide and phosphorus oxychloride, adds at the methylene carbon of the bidentate glycinate complex (p)-[Co(tren)(gly)](ClO₄)₂ to form the (p)-[Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]³⁺ ion. The crystal structure of the tetrachlorozincate chloride salt has been established by X-ray diffraction. Crystals of (p)-[Co^{III}(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]ZnCl₄·Cl·H₂O are monoclinic, space group $P2_1/n$, with $a = 14.608$ (3) Å, $b = 15.517$ (4) Å, $c = 10.562$ (2) Å, $\beta = 100.75$ (2)°, $V = 2352.1$ Å³, and $Z = 4$. Full-matrix least-squares refinement gave a final value of the conventional R factor of 0.035 (4631 reflections with $I > 3\sigma(I)$). The cation contains an approximately planar *cis*-3-(dimethylamino)-2-aminoacrylyl chloride ligand, the amine function of which is *trans* to the tertiary nitrogen of the tren ligand. Bond lengths in the framework of this bidentate ligand are (Cl)C-O = 1.267 (4), (Cl)C-C(NH₂) = 1.387 (5), (NH₂)C-C(H) = 1.387 (5), and C-N = 1.306 (4) Å, respectively, and provide evidence of considerable π -electron delocalization. The Co-O bond length is 1.936 (2) Å and the Co-N bond lengths range from 1.938 to 1.963 Å. The conformations adopted by the tren ligand are discussed. The Vilsmeier-Haack reaction has been carried out also on the complexes (t)-[Co(tren)(gly)](ClO₄)₂ and β_2 -[Co(tren)(gly)](ClO₄)₂ and a proposed mechanism for the reaction is discussed.

Introduction

The use of POCl₃ and disubstituted formamides to transfer a formyl group from the amide nitrogen to a substrate carbon atom has proved useful in organic syntheses since its discovery by Vilsmeier and Haack in 1927.⁴ A great range of substrates undergo this addition, including aromatic and heterocyclic com-

pounds, olefins, enamines, ketones, carboxylic acids, acetals, nitriles, and a variety of activated methylene compounds.⁵

(1) A paper presented at the 8th Coordination and Metal Organic Conference of the Royal Australian Chemical Institute, May 1978.

(2) The following abbreviations are used throughout this paper: tren, triethylenetetraamine (definition of α , β_1 , and β_2 as in ref 3); en, ethylenediamine; tren, tris(2-aminoethyl)amine; gly, bidentate glycinate ion; p and t refer to two geometrical isomers which arise in tren complexes due to the oxygen of the glycinate coordinating *trans* to the tertiary nitrogen (t) or the primary (p) nitrogen of the tren ligand.

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