

## A Planar Dodecasubstituted Porphyrin

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Structural investigations of copper and nickel complexes of dodecasubstituted porphyrins bearing aryl groups at the meso positions and propano rings at the pyrrole  $\beta$  positions reveal considerable differences in their macrocycle conformations. While the nickel complex NiTC5T(3,4,5-OMeP)P was found to exhibit a nonplanar conformation which is considerably more planar than that of other dodecasubstituted porphyrins, the corresponding copper complex CuTC5T(3,4,5-OMeP)P was planar. CuTC5T(3,4,5-OMeP)P thus represents the first example of a completely planar dodecasubstituted porphyrin. The crystal structures of both porphyrins reveal that the  $C_b-C_b-CH_2$  angle is  $13^\circ$  smaller than in OEP derivatives. This change, which moves the methylene and aryl substituents further apart, effectively removes the steric repulsion responsible for the very nonplanar conformations observed for other dodecasubstituted porphyrins. Molecular mechanics calculations using a porphyrin force field correctly predict a planar macrocycle conformation. The possible reasons for the discrepancy between the observed moderately nonplanar structure and the calculated planar structure for NiTC5T(3,4,5-OMeP)P are discussed. The usefulness of spectroscopic probes (NMR, resonance Raman, electronic absorption) in predicting the planarity of dodecasubstituted porphyrins is also examined. The identification of a planar dodecasubstituted porphyrin further indicates the flexibility of the tetrapyrrole macrocycle and has implications for the study of nonplanarity in synthetic porphyrins and metallotetrapyrrole containing biomolecules. Crystal data: NiTC5T(3,4,5-OMeP)P·2CH<sub>2</sub>Cl<sub>2</sub> (C<sub>68</sub>H<sub>68</sub>N<sub>4</sub>NiO<sub>12</sub>·2CH<sub>2</sub>Cl<sub>2</sub>), triclinic,  $P\bar{1}$ ,  $a = 14.492(8)$  Å,  $b = 14.453(8)$  Å,  $c = 17.689(10)$  Å,  $\alpha = 103.11(5)^\circ$ ,  $\beta = 113.58(4)^\circ$ ,  $\gamma = 89.93(5)^\circ$ ,  $V = 3290(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $T = 130$  K,  $R = 0.06$  for 7657 reflections with  $I > 2.5\sigma(I)$ ; CuTC5T(3,4,5-OMeP)P·CH<sub>2</sub>Cl<sub>2</sub> (C<sub>68</sub>H<sub>68</sub>N<sub>4</sub>CuO<sub>12</sub>·CH<sub>2</sub>Cl<sub>2</sub>), monoclinic,  $P2_1/c$ ,  $a = 14.459(4)$  Å,  $b = 15.302(6)$  Å,  $c = 14.879(4)$  Å,  $\beta = 100.68(4)^\circ$ ,  $V = 3235(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $T = 130$  K,  $R = 0.106$  for 4222 reflections with  $I > 2.0\sigma(I)$ .

## Introduction

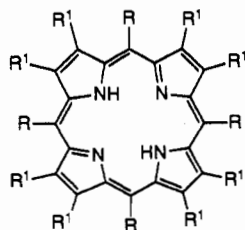
Porphyrins with distorted macrocycles have recently attracted wide interest as nonplanar macrocycle conformations have been found in tetrapyrrole-containing protein complexes *in vivo*.<sup>2</sup> Variation of the macrocycle conformation due to interaction with the apoprotein has been suggested to be responsible for fine-tuning the chromophore properties in protein complexes, thus giving rise to the variety of functional roles that similar cofactors can play in nature.<sup>3</sup> Dodecasubstituted porphyrins have been shown to be suitable model compounds for conformational studies since they are severely nonplanar due to steric crowding of the peripheral substituents.<sup>4-7</sup> They have also been implicated as useful compounds for biomimetic catalysis.<sup>8a,b</sup>

For a number of octaethyltetraphenylporphyrin (OETPP) derivatives, severely nonplanar conformations have been found

in the solid state and in solution.<sup>4-6,8b</sup> Intermediate degrees of nonplanarity have been described for a number of decasubstituted nickel(II) porphyrins.<sup>9</sup> The investigation of highly substituted porphyrins has been greatly facilitated by the development of a molecular mechanics force field for predicting the conformations of dodecasubstituted porphyrins.<sup>5,6,8b</sup> Using this method, the conformations of the nickel(II) complexes of octamethyltetraphenylporphyrin (OMTPP), OETPP, octapropyltetraphenylporphyrin (OPTPP), dodecaphenylporphyrin (DPP), tetraphenyltetrabutanoporphyrin (TC6TPP), and tetraphenyltetrapentanoporphyrin (TC7TPP) have been predicted to adopt nonplanar conformations. The validity of these predictions has

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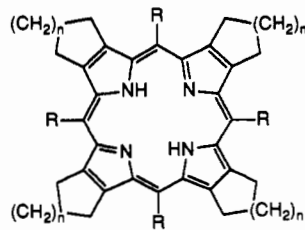


**OMTPP** R = C<sub>6</sub>H<sub>5</sub> R<sup>1</sup> = CH<sub>3</sub>

**OPTPP** R = C<sub>6</sub>H<sub>5</sub> R<sup>1</sup> = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

**OETPP** R = C<sub>6</sub>H<sub>5</sub> R<sup>1</sup> = CH<sub>2</sub>CH<sub>3</sub>

**DPP** R = R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>



**TC5TPP** n = 1 R = C<sub>6</sub>H<sub>5</sub>

**TC6TPP** n = 2 R = C<sub>6</sub>H<sub>5</sub>

**TC7TPP** n = 3 R = C<sub>6</sub>H<sub>5</sub>

**TC5TC5P** n = 1 R = pentyl

**TC5T(3,4,5-OMeP)P**  
n = 1 R = (3,4,5-OCH<sub>3</sub>)-C<sub>6</sub>H<sub>2</sub>

been demonstrated by crystallographic means.<sup>10</sup> The force field also correctly predicted the different distortion modes of (tetrapentyltetrapropanoporphinato)nickel(II) (NiTC5TC5P) (ruffled)<sup>11</sup> versus NiOETPP (saddle shaped).<sup>10,12</sup>

An interesting case was observed in the calculations for the structure of (tetraphenyltetrapropanoporphinato)nickel(II) (TC5TPP), which was predicted to be planar.<sup>5,6</sup> We were interested in obtaining unambiguous proof that highly substituted porphyrins can indeed be planar to further validate the force field employed for these calculations. Due to poor solubility we were not able to crystallize metal complexes of TC5TPP, but we were able to obtain satisfactory crystals of the nickel(II) and copper(II) complexes of tetrakis(3,4,5-trimethoxyphenyl)tetrapropanoporphyrin (TC5T(3,4,5-OMeP)P). We have employed X-ray crystallography, variable-temperature (VT) NMR, resonance Raman, and electronic absorption spectroscopy as well as molecular mechanics calculations to study the conformations of these compounds. Using these techniques, we show that the nickel complex exhibits a moderately nonplanar conformation, contrary to the calculated structure, while the corresponding copper complex CuTC5T(3,4,5-OMeP)P is planar and is in good agreement with calculations based on a force field<sup>8b</sup> for porphyrins. The structural factors which allow CuTC5T(3,4,5-OMeP)P to adopt a planar conformation are elucidated. The usefulness of spectroscopic probes of porphyrin nonplanarity is also investigated, with emphasis on the information these techniques can provide about the solution- and solid-state conformations of the TC5T(3,4,5-OMeP)P complexes. The difference between the experimentally observed and calculated structure for NiTC5T(3,4,5-OMeP)P is discussed.

## Experimental Section

**Synthesis.** TC5T(3,4,5-OMeP)P was prepared in 19% yield (unoptimized) from 3,4-propanopyrrole<sup>11</sup> and 3,4,5-trimethoxybenzaldehyde (Aldrich) using a procedure described previously.<sup>4</sup> The porphyrin was purified by column chromatography using Brockmann Grade III neutral alumina and 1% methanol in methylene chloride as eluent and was then crystallized from methylene chloride by addition of 2% KOH in ethanol.

- (10) Crystal structures of the nickel complexes of OETPP, OPTPP, and TC6TPP show very nonplanar saddle conformations (Barkigia, K. M.; Berber, M. D.; Fajer, J.; Furenid, L. R.; Medforth, C. J.; Renner, M. W.; Smith, K. M. Manuscript in preparation). The nickel complex of DPP could not be crystallized.
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**Table I.** Crystal Data and Data Collection Parameters for NiTC5T(3,4,5-OMeP)P and CuTC5T(3,4,5-OMeP)P

	NiTC5T(3,4,5-OMeP)P	CuTC5T(3,4,5-OMeP)P
chem formula	C <sub>68</sub> H <sub>68</sub> N <sub>4</sub> NiO <sub>12</sub> ·2CH <sub>2</sub> Cl <sub>2</sub>	C <sub>68</sub> H <sub>68</sub> N <sub>4</sub> CuO <sub>12</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
mol wt	1291	1257.8
space group	P $\bar{1}$	P2 <sub>1</sub> /c
a, Å	14.492(8)	14.459(4)
b, Å	14.453(8)	15.302(6)
c, Å	17.689(10)	14.879(4)
α, deg	103.11(5)	
β, deg	113.58(4)	100.68(4)
γ, deg	89.93(5)	
V, Å <sup>3</sup>	3290(3)	3235(2)
Z	2	2
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.303	1.309
μ(Mo Kα), mm <sup>-1</sup>	0.521	0.499
λ, Å	0.710 69	0.710 69
T, K	130	130
R	0.06	0.106
R <sub>w</sub>	0.083	0.146
S	1.33	0.43

Nickel(II) and copper(II) porphyrins were prepared using the acetate method<sup>13</sup> and were crystallized from methylene chloride by addition of methanol.

**Spectroscopic Measurements.** Proton NMR spectra were recorded at a frequency of 300 MHz on a General Electric QE-300 instrument. All chemical shifts are given in ppm and have been converted to the δ scale using the residual solvent signal at δ 5.30 for CD<sub>2</sub>Cl<sub>2</sub>. The variable-temperature unit was calibrated using a sample of methanol.<sup>14</sup> Electronic absorption spectra were recorded on a Hewlett Packard 8450A spectrophotometer using methylene chloride as solvent. Raman spectra were obtained using the 413.1-nm line from a Krypton ion laser (Coherent, Inc.) for excitation and a dual-channel Raman spectrophotometer described elsewhere.<sup>15</sup> The 150-μL aliquots of 1 × 10<sup>-4</sup> to 1 × 10<sup>-5</sup> M solutions in carbon disulfide of the porphyrin to be examined were placed in one side of a Raman cell. NiOETPP in carbon disulfide was used as the reference compound and was placed on the other side of the Raman cell. Laser power was typically 100 mW at the sample, and the cell was rotated at 50 Hz to prevent sample heating. Sample integrity was checked by visible spectroscopy before and after the Raman spectrum was recorded. Porphyrin photodegradation was not noted during the five to ten 25-minute scans required to obtain a spectrum. Frequencies were obtained from the peak positions of the lines in fast-FT smoothed spectra. For polycrystalline Raman spectra the spectrophotometer was used in the conventional single-channel mode and less than 10 mW of 413.1-nm light was used.

**X-ray Crystallography.** Crystals were grown by slow diffusion of methanol into a concentrated solution of the compound in methylene chloride. NiTC5T(3,4,5-OMeP)P crystallized in the form of black blocks while CuTC5T(3,4,5-OMeP)P gave red parallelepipeds. The crystals were immersed in hydrocarbon oil, and a single crystal was selected, mounted on a glass fiber, and placed in the low-temperature N<sub>2</sub> stream.<sup>16</sup> A Siemens R3m/V automatic diffractometer equipped with a graphite monochromator and a locally modified Siemens LT device was used. Graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) was used for data collection. The cell parameters were determined from 22 reflections with 20° ≤ 2θ ≤ 25° and are listed in Table I. The intensities were measured in the range 2θ = 0–55° at 130 K using the ω-scan technique. Two standard reflections were measured every 198 reflections and showed only statistical variation in intensity during the data collection. The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using the program XABS,<sup>17</sup> and extinction was disregarded. The structures were solved via Patterson

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**Table II.** Selected Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for NiTC5T(3,4,5-OMeP)P $\cdot$ 2CH $_2$ Cl $_2$ 

atom	x	y	z	$U(\text{eq})^a$	atom	x	y	z	$U(\text{eq})^a$
Ni	694(1)	3770(1)	2492(1)	12(1)	C(123)	483(3)	7697(3)	2690(3)	26(2)
N(21)	1138(2)	2527(2)	2535(2)	14(1)	C(13)	340(3)	6652(3)	2631(3)	17(1)
N(22)	-582(2)	3339(2)	2439(2)	15(1)	C(14)	747(3)	5785(3)	2392(2)	14(1)
N(23)	283(2)	5034(2)	2512(2)	15(1)	C(15)	1549(3)	5730(3)	2141(2)	14(1)
N(24)	1943(2)	4182(2)	2471(2)	13(1)	C(151)	1806(3)	6550(3)	1849(3)	17(1)
C(1)	2139(3)	2301(3)	2846(2)	15(1)	C(152)	1110(3)	6708(3)	1091(3)	22(2)
C(2)	2153(3)	1339(3)	2930(3)	16(1)	C(153)	1317(3)	7455(3)	791(3)	26(2)
C(21)	2872(3)	617(3)	3226(3)	20(2)	C(154)	2223(4)	8045(3)	1252(3)	27(2)
C(22)	2170(3)	-143(3)	3287(3)	25(2)	C(155)	2903(3)	7895(3)	2023(3)	22(2)
C(23)	1106(3)	-74(3)	2628(3)	25(2)	C(156)	2691(3)	7154(3)	2331(3)	18(2)
C(3)	1183(3)	955(3)	2607(3)	17(2)	C(157)	4467(4)	8410(3)	3221(4)	43(2)
C(4)	541(3)	1689(3)	2363(2)	14(1)	C(158)	2865(4)	8538(4)	366(3)	42(3)
C(5)	-500(3)	1606(3)	2081(3)	16(1)	C(159)	-236(4)	7062(4)	-426(3)	46(2)
C(51)	-1060(3)	632(3)	1764(3)	17(1)	C(16)	2123(3)	4960(3)	2183(2)	15(1)
C(52)	-1196(3)	110(3)	965(3)	21(2)	C(17)	3067(3)	4906(3)	2087(3)	16(1)
C(53)	-1732(3)	-785(3)	633(3)	24(2)	C(171)	3735(3)	5411(3)	1806(3)	21(2)
C(54)	-2128(3)	-1160(3)	1116(3)	24(2)	C(172)	4452(3)	4644(3)	1721(3)	25(2)
C(55)	-1994(3)	-632(3)	1923(3)	22(2)	C(173)	4506(3)	4040(3)	2347(3)	24(2)
C(56)	-1439(3)	270(3)	2257(3)	17(1)	C(18)	3498(3)	4161(3)	2397(3)	17(1)
C(57)	-1531(4)	-980(3)	-664(3)	38(2)	C(19)	2803(3)	3711(3)	2622(3)	16(1)
C(58)	-3626(5)	-2143(5)	165(4)	72(3)	C(20)	2938(3)	2867(3)	2900(2)	15(1)
C(59)	-2318(4)	-536(3)	3162(3)	34(2)	C(201)	3985(3)	2570(3)	3234(3)	16(1)
C(6)	-1032(3)	2396(3)	2139(3)	16(1)	C(202)	4664(3)	3068(3)	4029(3)	20(2)
C(7)	-2068(3)	2393(3)	2037(3)	18(1)	C(203)	5644(3)	2807(3)	4374(3)	24(2)
C(71)	-3008(3)	1725(3)	1750(3)	22(2)	C(204)	5935(3)	2052(3)	3911(3)	27(2)
C(72)	-3820(3)	2431(3)	1666(3)	26(2)	C(205)	5255(3)	1546(3)	3108(3)	22(2)
C(73)	-3267(3)	3380(3)	2316(3)	25(2)	C(206)	4275(3)	1815(3)	2760(3)	19(2)
C(8)	-2216(3)	3297(3)	2348(3)	18(2)	C(207)	4927(4)	299(3)	1922(3)	38(2)
C(9)	-1296(3)	3888(3)	2592(2)	14(1)	C(208)	7123(5)	1265(5)	4825(4)	65(3)
C(10)	-1191(3)	4880(3)	2844(3)	15(1)	C(209)	6080(4)	4044(4)	5640(3)	41(2)
C(101)	-1936(3)	5351(3)	3154(3)	17(1)	O(1)	-1924(3)	-1344(2)	-158(2)	36(1)
C(102)	-1913(3)	5237(3)	3914(3)	21(2)	O(2)	-2648(3)	-2056(2)	813(2)	41(2)
C(103)	-2584(3)	5667(3)	4236(3)	26(2)	O(3)	-2428(2)	-1055(2)	2336(2)	30(1)
C(104)	-3267(3)	6230(3)	3789(3)	24(2)	O(4)	-2615(3)	5599(3)	4981(2)	37(1)
C(105)	-3299(3)	6343(3)	3014(3)	22(2)	O(5)	-3936(2)	6674(2)	4097(2)	35(1)
C(106)	-2641(3)	5885(3)	2685(3)	19(2)	O(6)	-3996(2)	6902(2)	2626(2)	30(1)
C(107)	-1917(4)	5030(4)	5439(3)	43(2)	O(7)	3758(2)	8521(2)	2426(2)	32(1)
C(108)	-3499(4)	7557(3)	4713(3)	39(2)	O(8)	2431(3)	8800(2)	968(2)	39(2)
C(109)	-4097(4)	6992(3)	1806(3)	36(2)	O(9)	683(3)	7657(2)	45(2)	40(2)
C(11)	-433(3)	5429(3)	2804(2)	16(1)	O(10)	5609(2)	802(2)	2709(2)	34(1)
C(12)	-349(3)	6442(3)	2911(3)	17(1)	O(11)	6917(2)	1799(3)	4219(2)	42(2)
C(121)	-793(3)	7320(3)	3208(3)	22(2)	O(12)	6257(2)	3244(3)	5165(2)	39(1)
C(122)	-5(3)	8109(3)	3319(3)	26(2)					

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

synthesis, followed by structure expansion using the SHELXTL PLUS program system.<sup>18</sup> The solvent molecules were located in subsequent Fourier difference maps. The structure of CuTC5T(3,4,5-OMeP)P contains only half of the porphyrin macrocycle and a solvent molecule per asymmetric unit. The copper atom is located on a special position 0.5, 0, 0.5 and was refined with fixed coordinates in  $x$ ,  $y$ , and  $z$ . NiTC5T(3,4,5-OMeP)P crystallized with two molecules of solvation (CH $_2$ Cl $_2$ ). The refinement was carried out by full-matrix least-squares procedures on  $|F|$  using the same program system. Hydrogen atoms were included at calculated positions by using a riding model. Calculations were carried out on a Vax-station 3200. All non-hydrogen atoms were refined with anisotropic thermal parameters. Final  $R$  values for the observed data are listed in Table I, and additional refinement details are given in the supplementary material. Table II lists the atomic coordinates and isotropic temperature factors for NiTC5T(3,4,5-OMeP)P, while those for CuTC5T(3,4,5-OMeP)P are compiled in Table III.

Crystallization of NiCuTC5T(3,4,5-OMeP)P by diffusion of carbon tetrachloride into a solution of the porphyrin in methylene chloride gave small red plates, which crystallized in another form: C $_{68}$ H $_{68}$ -N $_4$ O $_2$ Ni $\cdot$ 8CCl $_4$ , triclinic,  $P\bar{1}$ ,  $a = 17.924(4)$  \AA,  $b = 18.295(6)$  \AA,  $c = 19.071(8)$  \AA,  $\alpha = 78.66(3)^\circ$ ,  $\beta = 62.48(3)^\circ$ ,  $\gamma = 65.74(2)^\circ$ ,  $V = 5056(3)$  \AA $^3$ ,  $Z = 2$ . Structure solution and expansion via Patterson synthesis revealed the positions of all atoms and showed that the porphyrin crystallized with eight (!) molecules of solvation (carbon tetrachloride) in the asymmetric unit. The high degree of disordering in the solvent

molecules and poor crystal quality gave a refinement convergence at  $R \approx 0.18$ . All further attempts to improve the refinement model were unsuccessful.

**Molecular Mechanics Calculations.** Molecular mechanics calculations using BIOGRAF software (Molecular Simulations, Inc.) were carried out and displayed on a Personal Iris 4D35 workstation (Silicon Graphics, Inc.). The basic Ni(II) porphyrin force field used for the calculations has been described previously.<sup>6</sup> The force constants were obtained from a normal-coordinate analysis for NiOEP<sup>19</sup> and the DREIDING force field.<sup>20</sup> The force field was parametrized such that it reproduced the crystal structure of the triclinic B form of NiOEP.<sup>21</sup> The current force field is only slightly different from that given previously,<sup>6</sup> in that it now employs an improper torsion term of the form  $E_\omega = \sum \gamma_\omega (1 - \cos \omega_0)$  and a cutoff distance of 50 \AA for nonbonding interactions. Parameters for copper(II) are those given by Sparks et al.<sup>5b</sup> Both planar and nonplanar conformations were used as starting points in the energy minimization procedure. The total calculated energy included contributions from bond stretching and bending, torsions, inversions (improper torsions), and van der Waals energies.

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 (21) Brennan, T. D.; Scheidt, W. R.; Shelnutz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919.

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**Table III.** Selected Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $\text{CuTC5T}(3,4,5\text{-OMeP})\text{P}\cdot\text{CH}_2\text{Cl}_2$ 

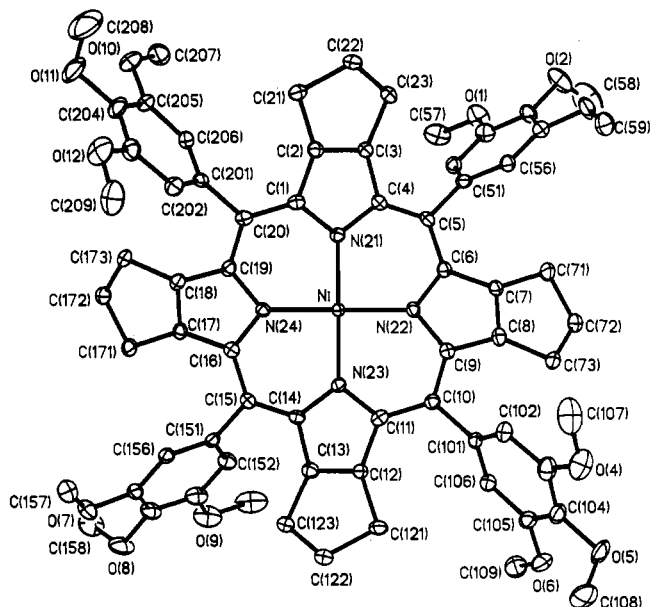
atom	x	y	z	$U(\text{eq})^a$
Cu	5000	0	5000	11(1)
N(1)	3859(3)	241(3)	4038(3)	13(1)
N(2)	4805(3)	1137(3)	5609(3)	15(2)
C(1)	3481(4)	-269(4)	3313(5)	15(2)
C(2)	2635(4)	122(4)	2797(4)	15(2)
C(21)	1892(6)	-38(6)	1966(6)	41(3)
C(22)	1291(5)	765(5)	1907(6)	33(2)
C(23)	1675(5)	1374(5)	2716(5)	31(2)
C(3)	2530(4)	892(4)	3197(4)	17(2)
C(4)	3290(4)	987(4)	3967(5)	17(2)
C(5)	3429(4)	1700(4)	4551(4)	14(2)
C(51)	2799(4)	2485(4)	4306(4)	18(2)
C(52)	3119(4)	3148(4)	3797(5)	23(2)
C(53)	2574(5)	3907(4)	3584(5)	23(2)
C(54)	1720(5)	3975(5)	3888(5)	26(2)
C(55)	1401(4)	3308(5)	4354(5)	23(2)
C(56)	1953(5)	2555(4)	4592(5)	22(2)
C(57)	3619(7)	4475(7)	2679(8)	54(4)
C(58)	1187(5)	5284(5)	4440(5)	27(2)
C(59)	147(5)	2702(6)	4969(6)	38(3)
C(6)	4111(4)	1762(4)	5334(4)	15(2)
C(7)	4212(4)	2465(4)	5974(5)	20(2)
C(71)	3731(5)	3305(5)	6163(5)	28(2)
C(72)	4438(5)	3705(5)	6938(5)	27(2)
C(73)	5118(4)	2979(5)	7368(4)	22(2)
C(8)	4973(4)	2292(4)	6646(5)	18(2)
C(9)	5342(4)	1466(4)	6410(4)	13(2)
C(10)	6143(4)	1069(4)	6906(4)	15(2)
C(11)	6670(4)	1559(4)	7711(4)	15(2)
C(12)	7363(4)	2154(5)	7570(4)	19(2)
C(13)	7825(4)	2650(5)	8310(5)	25(2)
C(14)	7595(4)	2547(5)	9179(5)	23(2)
C(15)	6935(4)	1932(5)	9310(5)	22(2)
C(16)	6464(4)	1436(4)	8587(4)	19(2)
C(17)	8809(7)	3288(9)	7375(7)	73(5)
C(18)	7480(6)	3793(6)	10048(6)	41(3)
C(19)	6159(7)	1217(7)	10376(6)	48(3)
O(1)	2830(4)	4588(4)	3109(4)	37(2)
O(2)	1191(3)	4745(3)	3680(4)	29(2)
O(3)	529(3)	3430(3)	4582(4)	32(2)
O(4)	8508(4)	3248(4)	8233(4)	39(2)
O(5)	8040(3)	3060(4)	9884(4)	40(2)
O(6)	6802(4)	1851(4)	10199(3)	36(2)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

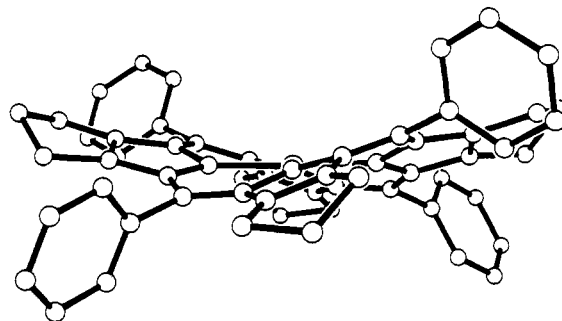
## Results and Discussion

A molecular mechanics force field<sup>5,6,8b,12</sup> has predicted with a high degree of accuracy the degree of nonplanarity and the type of distortion mode (for example pyrrole twisting or tilting) for a series of dodecasubstituted porphyrins. The dodecasubstituted porphyrins studied were all calculated to adopt very nonplanar conformations, except for  $\text{NiTC5TPP}$ , which was calculated to adopt a planar conformation.<sup>5,6</sup> As described above, we were only able to obtain crystals for the more soluble  $\text{TC5T}(3,4,5\text{-OMeP})\text{P}$  metal complexes. The molecular structure and numbering scheme for  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}$  are shown in Figure 1. Side views illustrate the macrocycle conformations of  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}$  (Figure 2) and of  $\text{CuTC5T}(3,4,5\text{-OMeP})\text{P}$  (Figure 3). Selected bond lengths, bond angles, and out-of-plane displacements are summarized in Table IV. The results of molecular mechanics calculations for  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}$  and  $\text{CuTC5T}(3,4,5\text{-OMeP})\text{P}$  are also given in Table IV. The methoxy substituents have a negligible effect on the calculated structure when compared to that of  $\text{NiTC5TPP}$ ; i.e. the out-of-plane displacements show that the minimum-energy structures for both  $\text{CuTC5T}(3,4,5\text{-OMeP})\text{P}$  and  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}$  are essentially planar.

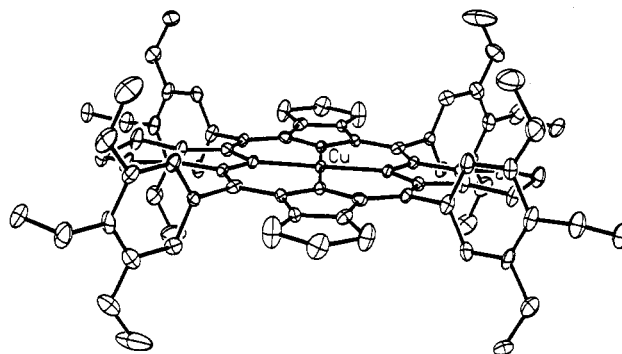
The experimentally determined core conformation in the crystal structure of  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}$  is moderately non-



**Figure 1.** Computer-generated plot of  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}\cdot 2\text{CH}_2\text{Cl}_2$  with labeling scheme used. Ellipsoids are drawn for 50% occupancy, and hydrogen atoms have been omitted for clarity.



**Figure 2.** Side view of  $\text{NiTC5T}(3,4,5\text{-OMeP})\text{P}\cdot 2\text{CH}_2\text{Cl}_2$  illustrating the nonplanar conformation of the macrocycle. The hydrogen atoms and the methoxy groups of the phenyl substituents have been omitted for clarity.



**Figure 3.** Computer-generated plot of the molecular structure of  $\text{CuTC5T}(3,4,5\text{-OMeP})\text{P}$ . Ellipsoids are drawn for 50% occupancy, and hydrogen atoms have been omitted for clarity.

planar in contrast to the calculated structure which is planar (possible reasons for this discrepancy are discussed later). On average, the 24 core atoms deviate from their least-squares plane by 0.36  $\text{\AA}$  (Figure 4A). The individual pyrrole rings are all planar within 0.02  $\text{\AA}$ . The conformation is characterized by ruffling, indicated by rotation of the pyrroles out of the macrocycle plane by 21.9° with an average angle of 30.5° between neighboring pyrrole rings, and some saddle deformation. The pyrrole  $\beta$  positions are displaced on average by 0.44  $\text{\AA}$ . The phenyl rings show considerable rotation (90–64 = 26°) away from the orthogonal orientation observed in planar tetraphenylporphyrins.<sup>12</sup>

The bond lengths and bond angles in the core region are typical

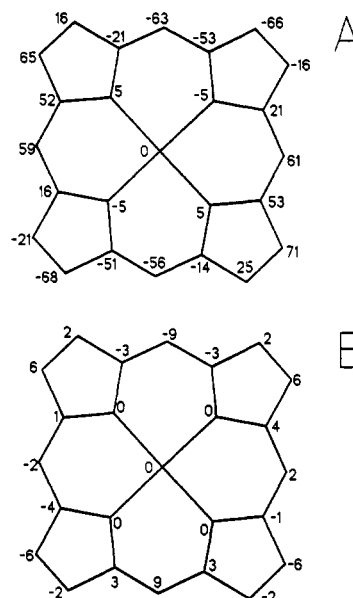
**Table IV.** Selected Structural Parameters of CuTC5T(3,4,5-OMeP)P and NiTC5T(3,4,5-OMeP)P and Comparison with Calculated Structural Parameters Using Force Fields for Nickel<sup>6</sup> and Copper<sup>8b</sup> Porphyrins

	CuTC5T(3,4,5-OMeP)P		NiTC5T(3,4,5-OMeP)P	
	exptl, planar conformn	calcd, planar conformn	exptl, ruffled/saddle conformn	calcd, planar conformn
Displacements <sup>a</sup> (Å)				
M	0.00	<0.01	0.00	<0.01
N	0.00	<0.01	0.05	<0.01
C <sub>a</sub>	0.06	<0.01	0.35	<0.01
C <sub>b</sub>	0.04	<0.01	0.44	<0.01
C <sub>m</sub>	0.06	<0.01	0.60	<0.01
Bond Lengths <sup>b</sup> (Å)				
M-N	2.007(5)	2.01	1.917(4)	1.97
N-C <sub>a</sub>	1.386(8)	1.40	1.390(5)	1.41
C <sub>a</sub> -C <sub>b</sub>	1.434(9)	1.44	1.435(6)	1.44
C <sub>a</sub> -C <sub>m</sub>	1.391(9)	1.39	1.389(6)	1.38
C <sub>b</sub> -C <sub>b</sub>	1.355(9)	1.29	1.350(6)	1.29
C <sub>b</sub> -CH <sub>2</sub>	1.501(10)	1.45	1.505(6)	1.45
CH <sub>2</sub> -CH <sub>2</sub>	1.527(11)	1.53	1.543(7)	1.53
C <sub>m</sub> -C <sub>ph</sub>	1.504(8)	1.41	1.495(6)	1.41
Bond Angles <sup>b</sup> (deg)				
N-M-N opp	90.0(2)	90.0	90.1(1)	90.0
N-M-N adj	180.0(1)	180.0	176.8(1)	180.0
M-N-C <sub>a</sub>	127.4(4)	126.6	127.0(3)	127.4
N-C <sub>a</sub> -C <sub>m</sub>	124.8(5)	126.9	124.1(3)	126.8
N-C <sub>a</sub> -C <sub>b</sub>	110.2(5)	107.2	109.7(3)	108.2
C <sub>a</sub> -N-C <sub>a</sub>	105.3(5)	106.8	105.5(3)	105.3
C <sub>a</sub> -C <sub>m</sub> -C <sub>a</sub>	125.5(5)	123.0	122.0(4)	121.8
C <sub>a</sub> -C <sub>b</sub> -C <sub>b</sub>	107.2(5)	109.4	107.5(4)	109.2
C <sub>m</sub> -C <sub>a</sub> -C <sub>b</sub>	125.0(5)	125.9	125.7(4)	125.1
C <sub>a</sub> -C <sub>b</sub> -CH <sub>2</sub>	140.8(6)	136.4	140.7(4)	136.6
C <sub>b</sub> -C <sub>b</sub> -CH <sub>2</sub>	112.0(6)	114.2	111.8(4)	114.2
C <sub>b</sub> -CH <sub>2</sub> -CH <sub>2</sub>	102.8(6)	101.4	100.9(4)	101.4
CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub>	108.7(6)	108.8	106.1(4)	108.7

<sup>a</sup> From least-squares planes of the four nitrogen atoms. <sup>b</sup> Average values of the geometrically equivalent positions.

for Ni(II) porphyrins with an S<sub>4</sub>-ruffled macrocycle.<sup>12,22</sup> However, it should be noted that the nonplanarity is not of the same order of magnitude observed in other highly substituted porphyrins. The displacement of the C<sub>b</sub> positions in the metal complexes of OETPP<sup>8b</sup> is on the order of 1.08–1.12 Å, i.e. more than double that in NiTC5T(3,4,5-OMeP)P. Similar crystallographic results were obtained with octabromotetraarylporphyrins<sup>8a</sup> and octaethyltetranitroporphyrins,<sup>8c</sup> while the distortion in DPP is even larger with C<sub>b</sub> displacements of up to 1.2 Å.<sup>11</sup> In fact, the degree of distortion for NiTC5T(3,4,5-OMeP)P is similar to that for the tetragonal form of Ni(II) octaethylporphyrin (OEP),<sup>23a</sup> which exhibits an alternate C<sub>m</sub> displacement of 0.51 Å above and below the mean plane and has the pyrrole rings tilted by about 14° with respect to the mean plane.<sup>23a</sup> Thus, the molecular mechanics calculations were correct in that they predicted that NiTC5T(3,4,5-OMeP)P should be more planar than dodecasubstituted porphyrins such as OETPP.<sup>8b</sup>

NiTC5T(3,4,5-OMeP)P was crystallized in two different crystal forms, one with two molecules of methylene chloride and the other with eight molecules of carbon tetrachloride.<sup>24</sup> The distortion modes are quite similar in both compounds, but the degree of distortion is about 15% smaller in NiTC5T(3,4,5-



**Figure 4.** Deviations from the least-squares planes of the four nitrogen atoms in NiTC5T(3,4,5-OMeP)P-2CH<sub>2</sub>Cl<sub>2</sub> (A) and CuTC5T(3,4,5-OMeP)P-CH<sub>2</sub>Cl<sub>2</sub> (B).

OMeP)P-8CCl<sub>4</sub> than in NiTC5T(3,4,5-OMeP)P-2CH<sub>2</sub>Cl<sub>2</sub>. Unfortunately the high number of solvent molecules prevented a detailed analysis of the structural properties of NiTC5T(3,4,5-OMeP)P-8CCl<sub>4</sub>. The fact that multiple crystal modifications for a number of porphyrins are known points to the high degree of conformational flexibility of tetrapyrroles.<sup>3b,c,11,25</sup> This indicates the crucial importance of analyzing a given structure for packing and  $\pi$ - $\pi$  interaction effects, which can play important roles in modifying the macrocycle conformation.<sup>11</sup> The second crystalline form of NiTC5T(3,4,5-OMeP)P is further evidence that it is more like an essentially "planar" porphyrin such as NiOEP rather than a conformationally constrained nonplanar porphyrin such as NiOETPP.

The copper complex CuTC5T(3,4,5-OMeP)P crystallized with one molecule of solvation (methylene chloride). The copper atom is situated on a crystallographic inversion center; thus only half of the molecule is present in the asymmetric unit. The macrocycle of CuTC5T(3,4,5-OMeP)P is evidently planar, in complete agreement with the calculations (Figure 3). Thus, it is a unique example of a planar dodecasubstituted porphyrin. The average deviation from the least-squares plane is 0.03 Å for the 24 macrocycle atoms. The plane of the four nitrogen atoms (4N plane) is perfectly planar (Figure 4B). The angles between individual pyrroles and the 4N plane are 1.9°, while neighboring pyrroles are twisted against each other by only 3.7°. The meso aryl groups are almost orthogonal to the plane of the macrocycle, with an angle of 87.4° between the aryl plane and the 4N plane. The bond lengths and bond angles in the core region agree well with those observed in other planar copper(II) porphyrins.

The crystal structures of CuTC5T(3,4,5-OMeP)P and NiTC5T(3,4,5-OMeP)P reveal why there is so little steric strain between the peripheral substituents. The answer lies in the small internal angles of the fused five-membered rings. As a consequence the C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> bond angle is only 111.8(4)° for CuTC5T(3,4,5-OMeP)P compared with a more typical octaalkyltetraarylporphyrin angle of 125.0° (e.g. in the very nonplanar CuOETPP).<sup>8b</sup> NiOEP has also C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> angles of about 125°.<sup>23</sup> The smaller C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> bond angles indicate that

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 (23) (a) Meyer, E. F., Jr. *Acta Crystallogr.* **1972**, *B28*, 2162. (b) Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2095. (c) Brennan, T. D.; Scheidt, W. R.; Shelnut, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919.  
 (24) Note that the crystal structure of NiTC5T(3,4,5-OMeP)P-8CCl<sub>4</sub> could not be refined satisfactorily and thus the deviations from planarity given here are only an indication of the overall degree of distortion.

- (25) (a) Sparks, L. D.; Scheidt, W. R.; Shelnut, J. A. *Inorg. Chem.* **1992**, *31*, 2191. (b) Stolzenberg, A. M.; Glazer, P. A.; Foxman, B. M. *Inorg. Chem.* **1986**, *25*, 983. Senge, M. O.; Ruhlandt-Senge, K.; Smith, K. M. *Acta Crystallogr.* **1992**, *C48*, 1810. Senge, M. O.; Hope, H.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 11. (c) See ref 21 and references therein.



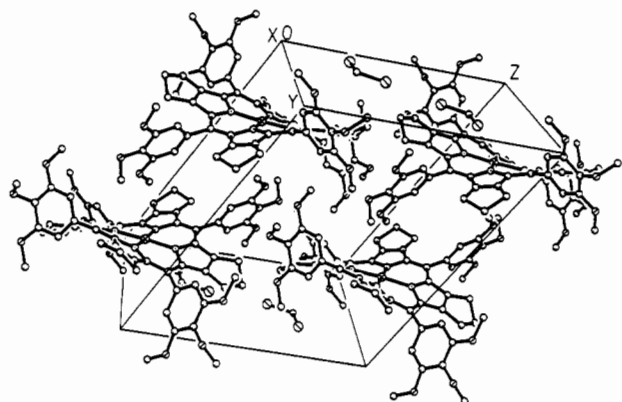


Figure 5. View of the molecular packing in the unit cell of NiTC5T(3,4,5-OMeP)P·2CH<sub>2</sub>Cl<sub>2</sub>.

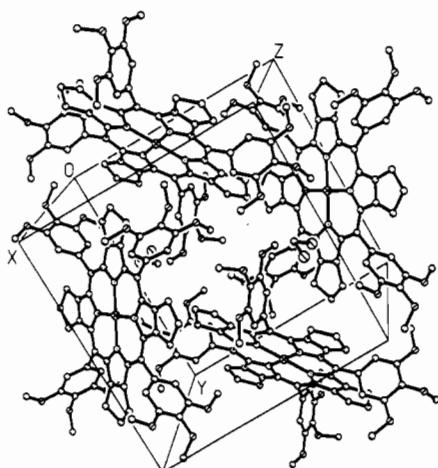


Figure 6. View of the molecular packing in the unit cell of CuTC5T(3,4,5-OMeP)P·CH<sub>2</sub>Cl<sub>2</sub>.

the methylene groups are effectively moved away from the meso aryl groups, thus decreasing the steric interactions which are responsible for a nonplanar conformation. In agreement with this mechanism for modifying macrocyclic nonplanarity, a preliminary crystal structure analysis of CuTC6TPP reveals a moderately nonplanar saddle conformation and a C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> bond angle of about 123°. It should also be noted that the structure of NiTC5T(3,4,5-OMeP)P exhibits C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> bond angles of 112.0(6)°, suggesting that the observed distortion of the macrocycle arises mainly from the effect of the small nickel(II) ion and not from steric repulsion of the peripheral substituents.

The molecular mechanics calculations show a decrease in van der Waals energy for NiTC5TPP compared to the highly nonplanar dodecasubstituted porphyrins, as is expected for a reduction in peripheral steric strain.<sup>6</sup> The calculations also reproduce the experimentally observed change in the C<sub>b</sub>-C<sub>b</sub>-CH<sub>2</sub> angle. The agreement between observed and calculated structural parameters for CuTC5T(3,4,5-OMeP)P is quite accurate (Table IV). The parameters for the core region are almost identical while some deviations are observed in the C<sub>b</sub>-C<sub>b</sub> bond lengths and bond angles involving the C<sub>b</sub> atoms. The differences between observed and calculated C<sub>b</sub>-C<sub>b</sub> and C<sub>b</sub>-CH<sub>2</sub> bond lengths may reflect the fact that no special five-membered ring parameters were used in the calculations. The much shorter calculated versus observed C<sub>m</sub>-C<sub>ph</sub> bond is likely due to the force field treating this as a standard sp<sup>2</sup>-sp<sup>2</sup> bond even though there is very little π overlap because the two systems are almost orthogonal. With respect to predicting porphyrin geometries in protein-porphyrin complexes, it is encouraging to note the good agreement between the predicted and experimental structures for the copper complex.

(26) Senge, M. O.; Medforth, C. J.; Smith, K. M. Unpublished results.

Table V

(a) NMR Data for TC5T(3,4,5-OMeP)P (ppm)						
proton	free base <sup>a</sup>		Ni complex <sup>a</sup>		dication <sup>b</sup>	
	293 K	193 K	293 K	188 K	294 K	189 K
ortho H	7.21	7.11	7.05	6.98	7.46	7.40
meta OCH <sub>3</sub>	3.86	3.75	3.83	3.75	4.00	3.93
para OCH <sub>3</sub>	4.05	3.96	4.00	3.92	4.11	4.06
α CH <sub>2</sub>	3.00	3.02	2.93	2.85	2.97	3.29
β CH <sub>2</sub>	2.56	2.79	2.40	2.31	2.49	2.62
		2.50			2.16	
NH	-3.86	-4.19			-2.37	-3.05

(b) ΔG° for Macrocyclic Inversion Obtained from NMR Experiments (kJ mol<sup>-1</sup>)<sup>c</sup>

	free-base porphyrin	porphyrin dication	Ni(II) porphyrin
TC5TPP	<i>d</i>	47.7	<i>d</i>
TC5T(3,4,5-OMeP)P	<29	46.4	<29
TC6TPP	35 <sup>d</sup>	>84	<33
TC7TPP	67	>84	49
OETPP	76	>84	55

<sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> CD<sub>2</sub>Cl<sub>2</sub>/1% trifluoroacetic acid. <sup>c</sup> All data except those for NiTC5T(3,4,5-OMeP)P were taken from ref 5. <sup>d</sup> The porphyrin was not sufficiently soluble in a suitable solvent. <sup>e</sup> We were unable to obtain a slow-exchange spectrum due to the low energy barrier for this process, although this process is most likely macrocyclic inversion. The value of ΔG° has been estimated.

Table VI. Resonance Raman Data for Nickel and Copper Porphyrins (cm<sup>-1</sup>)

	solution		polycrystalline	
	ν <sub>3</sub>	ν <sub>2</sub>	ν <sub>3</sub>	ν <sub>2</sub>
NiTC5TPP	1525.7	1586.5	1528.2	1591.0
NiTC5T(3,4,5-OMeP)P	1524.3	1584.7	1522.1	1578.0
NiTC6TPP	1512.9	1576.9	1512.8	1572.6
NiOETPP	1504.7	1562.0	1507.0	1565.8
CuTC5T(3,4,5-OMeP)P	1511.3	1575.1	1511.4	1575.8

The structural differences between the planar CuTC5T(3,4,5-OMeP)P and nonplanar NiTC5T(3,4,5-OMeP)P are roughly the same as those seen for the corresponding OEP structures.<sup>12</sup> There is a decrease in the M-N distance and a decrease in the C<sub>a</sub>-M-C<sub>a</sub> angle as the core size becomes smaller. The mean angle between the aryl planes and 4N plane also decreases to 63.6° for the nonplanar nickel complex. A much larger decrease is seen for the very nonplanar dodecasubstituted porphyrins such as NiOETPP and CuOETPP, where this angle is approximately 46°. However the angles between the C<sub>a</sub>-C<sub>m</sub>-C<sub>a</sub> and C<sub>o</sub>-C<sub>i</sub>-C<sub>o</sub> planes, which are a better measure of overlap between the phenyl and porphyrin π systems are 88.3° for CuTC5T(3,4,5-OMeP)P, 70.6° for NiTC5T(3,4,5-OMeP)P, and 67.4° for CuOETPP.<sup>8b</sup> Thus it is easy to see why there is negligible shortening of the C<sub>m</sub>-C<sub>i</sub> bond even in very nonplanar porphyrins.<sup>4,8b,11</sup>

No evidence for π-π interaction between neighboring molecules was found in either structure. Figures 5 and 6 display the arrangements of the porphyrin and solvent molecules in the unit cells of NiTC5T(3,4,5-OMeP)P·2CH<sub>2</sub>Cl<sub>2</sub> and CuTC5T(3,4,5-OMeP)P·CH<sub>2</sub>Cl<sub>2</sub>. The nickel porphyrins (Figure 5) pack in parallel layers with the solvent molecules acting as spacers between layers. The Ni-Ni distances between neighboring molecules are 12.01 Å within a layer and 9.77 Å to the next layer above or below. No porphyrin-porphyrin contacts <4 Å were found. However, there are some contacts between the solvent molecules (methylene chloride) and porphyrin macrocycles on the order of 3.8-4.6 Å. The shortest contact is found to be 3.78 Å between C(12) and Cl(1). It is difficult to rationalize these contacts as being responsible for the conformational distortion observed.

**Table VII.** Absorption Maxima for TPP and Dodecasubstituted Porphyrins (nm)

	free-base porphyrin <sup>a</sup>	porphyrin dication <sup>b</sup>	Ni(II) porphyrin <sup>c</sup>
TPP	414, 514, 548, 588, 646	438, 522, 600, 650	414, 525, 557
TC5TPP	414 <sup>d</sup>	434, 536, 580, 632	413 <sup>d</sup>
TC5T(3,4,5-OMeP)P	414, 508, 544, 580, 634	444, 536, 580, 636	408, 522, 554
TC6TPP	438, 536, 580, 610, 678	458, 558, 612, 668	424, 543, 579
TC7TPP	464, 558, 600, 630, 704 <sup>e</sup>	474, 578, 632, 700	440, 556, 595
OETPP	456, 554, 600, 640, 706	472, 580, 640, 694	432, 552, 558

<sup>a</sup> In methylene chloride (plus 1% triethylamine for nonplanar porphyrins). <sup>b</sup> In methylene chloride plus 1% trifluoroacetic acid. <sup>c</sup> In methylene chloride. <sup>d</sup> Saturated solution—other bands too weak to observe. <sup>e</sup> In benzene.

The CuTC5T(3,4,5-OMeP)P molecules pack quite differently (Figure 6). Two series of porphyrin layers are closely packed to form a network of molecules in which the macrocycles of neighboring molecules are oriented almost orthogonal to each other. The Cu–Cu distance between molecules within a layer is 14.46 Å, while the distance between copper atoms in molecules rotated against each other is 10.67 Å. No  $\pi$ – $\pi$  interactions of the macrocycles in one layer are observed. Also, no  $\pi$ – $\pi$  interaction of neighboring phenyl rings was found. The closest contact was found to be 3.85 Å between a methoxy carbon [C(59)] and a methylene bridge [C(22)] of one of the five-membered rings. All other intermolecular distances were >4 Å.

In light of these results, it is interesting to examine the use of molecular mechanics calculations in predicting porphyrin structures. The force field clearly works for predicting the structures of the very nonplanar dodecasubstituted porphyrins, and it also correctly predicts a planar structure for CuTC5T(3,4,5-OMeP)P. However, the force field does not predict a nonplanar structure for NiTC5T(3,4,5-OMeP)P, nor does it predict the ruffled, tetragonal form of NiOEP.<sup>27</sup> One explanation for this fact is that the force field cannot reproduce crystal packing effects. Furthermore, a nonplanar structure may only be obtained as a minimum energy structure if there is a barrier between the planar and nonplanar forms. Thus it is not surprising that the force field fails to predict the structure of NiTC5T(3,4,5-OMeP)P.

In addition to structural studies, several spectroscopic techniques have recently been used to probe the effects of porphyrin nonplanarity using dodecasubstituted porphyrins.<sup>4–7,8b</sup> We decided to investigate the conformation of TC5T(3,4,5-OMeP)P in solution, using variable-temperature NMR spectroscopy. The NMR data for the free base, dication, and nickel complex of TC5T(3,4,5-OMeP)P are summarized in Table V. The spectrum of NiTC5T(3,4,5-OMeP)P is consistent with a planar structure down to the lowest temperature studied, even though a nonplanar structure is seen in the crystalline state. NH tautomerism was the only dynamic process detected for the free base porphyrin; otherwise the NMR spectrum was also consistent with a planar conformation. Using the standard equation,<sup>28</sup>  $\Delta G^*$  for NH tautomerism was calculated to be 56.8 kJ mol<sup>-1</sup>, which is similar to the value found for TPP.<sup>29</sup> In contrast, the dication was found to be nonplanar in solution, with the methylene protons being diastereotopic at low temperatures but equivalent at room temperature. This dynamic process has previously been characterized as a type of porphyrin macrocyclic inversion.<sup>5</sup>

The activation energies for this process and the macrocyclic inversion processes observed for the free bases, dications, and nickel complexes of TC5TPP, TC6TPP, TC7TPP, and OETPP are given in Table V. Higher values of  $\Delta G^*$  are expected and seen for more nonplanar porphyrins like OETPP. However, NiTC5TPP and NiTC5T(3,4,5-OMeP)P behave, from an NMR standpoint, like “planar” porphyrins. In the case of NiTC6TPP this is almost certainly the case because the barrier for macrocyclic

inversion is too low to permit the detection of a nonplanar conformation, as this porphyrin adopts a very nonplanar saddle conformation in the crystalline state.<sup>10</sup> NMR spectroscopy is therefore a somewhat unreliable predictor of porphyrin nonplanarity and can only be employed when the barrier to macrocyclic inversion is sufficiently large.

Raman spectroscopy can also be used as an indicator of nonplanarity in porphyrins.<sup>5,6,8b</sup> For example, both planar and nonplanar forms of NiOEP have been found to coexist in solution on the basis of the frequencies of a group of structure-sensitive Raman lines.<sup>27</sup> The Raman data for NiTPP, NiTC5TPP, NiTC5T(3,4,5-OMeP)P, NiTC6TPP, NiTC7TPP, NiOETPP, and CuTC5T(3,4,5-OMeP)P are summarized in Table VI. A correlation is observed between the degree of nonplanarity expected for the nickel complexes and the frequencies of  $\nu_2$  and  $\nu_3$  (in cm<sup>-1</sup>) for both the solution and crystal/powder data.<sup>6</sup> The data for CuTC5T(3,4,5-OMeP)P in solution and in the crystalline state are almost identical, suggesting that it has a planar conformation in solution and in the crystalline state. Typically, slightly higher frequencies (1–2 cm<sup>-1</sup>) are observed in the crystalline state, assuming no structural variation between the solution and crystalline phases. In contrast, the peak frequencies for NiTC5T(3,4,5-OMeP)P in the solid state are decreased compared to the values seen in solution, suggesting a more nonplanar conformation than in solution. The low solid-state frequencies for NiTC5T(3,4,5-OMeP)P are consistent with a nonplanar structure but are at somewhat higher frequencies than would be expected for a conformation as nonplanar as is observed in the crystal structure (Figure 2).

It is also interesting to compare the Raman and structural data for NiTC5TPP and NiTC5T(3,4,5-OMeP)P. The positions of  $\nu_2$  and  $\nu_3$  for NiTC5T(3,4,5-OMeP)P and NiTC5TPP are very similar in solution. However, in the solid state  $\nu_2$  and  $\nu_3$  for NiTC5TPP shift to higher values whereas for NiTC5T(3,4,5-OMeP)P they shift to lower values. The high solid-state frequencies for NiTC5TPP indicate a planar conformation, consistent with preliminary EXAFS data (Ni–N bond distance of 1.99(2) Å).<sup>10</sup> The low solution values observed for NiTC5TPP may be a result of the typically lower values observed in the solution spectra. Alternatively, the low frequencies observed in the NiTC5TPP solution spectra may arise from a conformation of intermediate nonplanarity or a superposition of the spectra of two or more conformations as was observed for NiOEP.<sup>27</sup> We have addressed the latter possibility by simulating  $\nu_2$  and  $\nu_3$  using a nonlinear least-squares curve fitting program.<sup>30</sup> Lorentzian line shapes were employed in the least-squares fits for  $\nu_2$  for the solution spectra of NiTC5T(3,4,5-OMeP)P and CuTC5T(3,4,5-OMeP)P. The results of the fits show somewhat broader lines for NiTC5T(3,4,5-OMeP)P (12.8 ± 1.3 cm<sup>-1</sup>) than for CuTC5T(3,4,5-OMeP)P (9.3 ± 0.8 cm<sup>-1</sup>), possibly indicating the presence of multiple conformers in solution for NiTC5T(3,4,5-OMeP)P.

Nonplanarity also causes a shift to absorption at lower energy in the optical spectra of dodecasubstituted metalloporphyrins.<sup>3b</sup> The optical spectra of TC5T(3,4,5-OMeP)P complexes should

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therefore resemble those of a planar porphyrin (such as TPP) rather than a highly nonplanar dodecasubstituted porphyrin such as OETPP. The absorption maxima of TC5T(3,4,5-OMeP)P derivatives and some highly nonplanar porphyrins show that this is the case (Table VII). However, as the TPP dication adopts a very nonplanar structure in the crystalline state<sup>31</sup> one might expect the dications not to show the same pattern of red shifts as the free bases or nickel complexes. (In the crystalline state, the OETPP dication is only slightly more nonplanar than the TPP dication.<sup>32</sup>) The fact that they do seems to imply that in solution the peripheral substituents impose an additional nonplanar distortion beyond that caused by protonation. Thus,

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electronic absorption spectroscopy gives a rather crude but nevertheless important indication of the macrocycle conformation in solution.

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**Supplementary Material Available:** Listings of structure determination details and complete bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and a figure showing the atom-labeling scheme for CuTC5T(3,4,5-OMeP)P (17 pages). Ordering information is given on any current masthead page.