# Crystal and Molecular Structure of the Triclinic Form of 1,2,3,4,5,6,7,8-Octaethylporphinatonickel(II). A Comparison with the Tetragonal Form

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**Abstract:** The structure of a triclinic crystalline form of 1,2,3,4,5,6,7,8-octaethylporphinatonickel(II) has been determined from three-dimensional X-ray counter data. The crystals, grown from a pyridine–dioxane solution, have the space group $P\bar{1}$ with a unit cell of $a = 9.924$ (3) Å, $b = 10.564$ (3) Å, $c = 7.617$ (2) Å, $\alpha = 97.66$ (2)°, $\beta = 109.47$ (3)°, and $\gamma = 92.35$ (3)° with one molecule per unit cell. The observed and calculated densities are 1.31 (1) and 1.322 g/cm³, respectively. The structure was solved by Fourier methods and refined by least-squares techniques to a final conventional $R$ factor of 0.045 (based on $F$) for the 2080 reflections having $I > 3\sigma_I$. The metalloporphyrin is a centrosymmetric square-planar complex with Ni–N bond lengths of 1.957 (2) and 1.959 (2) Å. The macrocycle is effectively planar with an angle between the planes of adjacent pyrrole rings of 2.1°. There are marked differences between the structure in the triclinic crystalline form and in the tetragonal crystalline form of the same complex, particularly in the degree of nonplanarity of the porphinato core. Packing calculations seem to indicate the tetragonal modification is the lower energy form.

Recently the structure determination of a tetragonal form of 1,2,3,4,5,6,7,8-octaethylporphinatonickel-(II) (NiOEP) has been published.[1] There are two unusual features about this square-planar complex. The Ni–N distance is the shortest M–N bond yet reported for a metalloporphyrin, and the macrocycle is highly distorted, having in effect $D_{2d}$ symmetry. The angle between planes of adjacent pyrrole rings is 32.8°. Hoard[2] has made extensive use of the data on this complex to examine the correlation between M–N distances and the geometry of the macrocycle in metalloporphyrins.

The crystals of tetragonal NiOEP were grown from a mixture of benzene, nitromethane, and dichloromethane. More recently in an attempt to prepare a high spin Ni(II) complex, NiOEP was dissolved in a 1:1 pyridine–dioxane solution. Crystals of markedly different habit from the tetragonal bipyramids of the tetragonal NiOEP were obtained. The material proved to be a triclinic crystalline modification of NiOEP. The structure has been determined by three-dimensional X-ray diffraction methods. Like the tetragonal form, the triclinic form contains four-coordinate square-planar metalloporphyrin molecules, but there are some marked differences in structural details. In the triclinic form the porphyrin moiety is essentially planar and the Ni–N distance is the same as found for other nickel(II) metalloporphyrins.

A comparison of the two crystalline forms of NiOEP provides an ideal opportunity to study the correlation between M–N distances and the geometry of the macrocycle, since other factors such as different substituents on the ring, which also affect the geometry, are eliminated. It is also of interest to compare the two forms of NiOEP with the recently determined structure of the free base of octaethylporphyrin,[3] which is virtually isomorphous with triclinic NiOEP, and with the structure

of the square-planar complex, $\alpha,\beta,\gamma,\delta$-tetrapropylporphinatocopper(II).[4]

## Experimental Section

Samples of 1,2,3,4,5,6,7,8-octaethylporphinatonickel(II) were supplied by Dr. David Dolphin of Harvard University. Crystals of the triclinic form of NiOEP were grown from a 1:1 pyridine–dioxane solution by very slow cooling. In contrast to the bipyramidal form exhibited for the tetragonal modification, crystals of the triclinic form were rods elongated along $c$, and bounded by {100} and {010}. The crystal used for intensity collection was cleaved from a larger crystal. The approximate dimensions of the crystal were 0.20 and 0.10 mm in the direction of $a$ and $b$, respectively, while the mean distance along $c$ was 0.24 mm.

Cell data for triclinic NiOEP are summarized in Table I. For

**Table I.** Crystal Data for Nickel(II) Octaethylporphyrin[a]

|  | Tetragonal | Triclinic |
|---|---|---|
| $a$ | 14.93 (1) Å | 9.924 (3) Å |
| $b$ | 14.93 (1) Å | 10.564 (3) Å |
| $c$ | 13.84 (1) Å | 7.617 (2) Å |
| $\alpha$ | 90.0° | 97.66 (2)° |
| $\beta$ | 90.0° | 109.47 (3)° |
| $\gamma$ | 90.0° | 92.35 (3)° |
| Volume | 3085 Å³ | 743.0 Å³ |
| $D_{calcd}$ | 1.27 g/cm³ | 1.32 g/cm³ |
| $D_{measd}$ | 1.27 (1) g/cm³ | 1.31 (1) g/cm³ |
| Mol wt | 591.5 daltons | 591.5 daltons |
| $Z$ | 4 | 1 |
| Space group | $I4_1/a$ | $P\bar{1}$ |
| $\mu$ | 6.61 cm⁻¹ | 6.87 cm⁻¹ |

[a] Estimated standard deviations in parentheses.

purposes of comparison, the values obtained for the tetragonal form are also listed. Cell dimensions were determined by least squares, minimizing the differences between observed and calculated $2\theta$ values for 34 reflections. The ambient temperature was 20°. The density was determined by the flotation method in an aqueous potassium iodide solution. It should be noted that the triclinic form has a higher density than the tetragonal form. The choice of $P\bar{1}$ as the space group rather than $P1$ was confirmed by the successful solution of the structure.

(1) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **28**, 2162 (1972).
(2) J. L. Hoard, *Ann. N. Y. Acad. Sci.*, **206**, 18 (1973).
(3) J. W. Lauher and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 5148 (1973).
(4) I. Moustakali and A. Tulinsky, *J. Amer. Chem. Soc.*, **95**, 6811 (1973).

**Table II.** Fractional Coordinates and Thermal Motion Parameters Derived from the Least-Squares Refinement[a]

| Atom | $x$ | $y$ | $z$ | $U(11)$[b] | $U(22)$ | $U(33)$ | $U(12)$ | $U(13)$ | $U(23)$ |
|------|-----|-----|-----|---------|---------|---------|---------|---------|---------|
| NI | 0.0000 | 0.0000 | 0.0000 | 342 (3) | 344 (3) | 310 (3) | 16 (2) | 25 (3) | 53 (2) |
| N(1) | 0.1172 (2) | 0.0103 (2) | 0.2663 (3) | 348 (14) | 344 (15) | 312 (15) | 5 (12) | 20 (12) | 69 (12) |
| N(2) | 0.0964 (2) | 0.1631 (2) | −0.0089 (3) | 387 (15) | 364 (14) | 336 (16) | 13 (12) | 42 (13) | 73 (13) |
| C(1) | 0.1139 (3) | −0.0745 (2) | 0.3860 (4) | 385 (18) | 401 (18) | 377 (19) | 56 (15) | 85 (15) | 68 (16) |
| C(2) | 0.2149 (3) | −0.0322 (3) | 0.5737 (4) | 426 (19) | 464 (19) | 330 (18) | 95 (16) | 82 (15) | 81 (16) |
| C(3) | 0.2829 (3) | 0.0793 (2) | 0.5672 (4) | 399 (19) | 414 (19) | 349 (18) | 66 (15) | 27 (15) | 8 (16) |
| C(4) | 0.2222 (3) | 0.1053 (2) | 0.3761 (4) | 386 (18) | 366 (18) | 358 (18) | 56 (14) | 35 (15) | 14 (15) |
| C(5) | 0.2639 (3) | 0.2102 (2) | 0.3129 (4) | 451 (20) | 366 (18) | 440 (20) | −63 (15) | −24 (17) | −11 (16) |
| C(6) | 0.2064 (3) | 0.2376 (3) | 0.1328 (4) | 409 (19) | 392 (18) | 424 (20) | 8 (15) | 44 (16) | 52 (16) |
| C(7) | 0.2518 (3) | 0.3491 (2) | 0.0699 (4) | 454 (20) | 406 (19) | 493 (21) | −59 (16) | 57 (17) | 91 (17) |
| C(8) | 0.1695 (3) | 0.3439 (3) | −0.1118 (4) | 422 (19) | 442 (20) | 497 (21) | −35 (16) | 85 (17) | 115 (17) |
| C(9) | 0.0738 (3) | 0.2281 (3) | −0.1603 (4) | 427 (19) | 417 (19) | 400 (19) | 34 (15) | 105 (16) | 92 (16) |
| C(10) | −0.0252 (3) | 0.1858 (3) | −0.3364 (4) | 481 (21) | 498 (21) | 394 (20) | 46 (17) | 99 (17) | 206 (18) |
| C(11) | 0.2391 (3) | −0.1028 (3) | 0.7368 (4) | 585 (23) | 563 (22) | 372 (20) | 100 (18) | 152 (18) | 94 (17) |
| C(12) | 0.3407 (4) | −0.2064 (3) | 0.7409 (5) | 694 (26) | 677 (26) | 507 (24) | 195 (21) | 122 (21) | 272 (21) |
| C(13) | 0.4025 (3) | 0.1606 (2) | 0.7215 (4) | 573 (22) | 488 (20) | 358 (19) | 12 (17) | 0 (17) | −2 (17) |
| C(14) | 0.5509 (3) | 0.1258 (3) | 0.7278 (4) | 480 (21) | 670 (24) | 527 (23) | −35 (19) | −6 (18) | −15 (20) |
| C(15) | 0.3716 (4) | 0.4489 (3) | 0.1869 (6) | 585 (26) | 530 (25) | 602 (28) | −81 (21) | 86 (22) | 100 (22) |
| C(16) | 0.3298 (4) | 0.5450 (3) | 0.3160 (6) | 743 (28) | 586 (24) | 904 (33) | −106 (22) | 111 (26) | 24 (25) |
| C(17) | 0.1703 (4) | 0.4388 (3) | −0.2396 (5) | 553 (24) | 656 (27) | 626 (28) | −155 (21) | 44 (22) | 247 (24) |
| C(18) | 0.0747 (4) | 0.5439 (4) | −0.2282 (6) | 871 (32) | 873 (31) | 1298 (43) | 163 (27) | 297 (32) | 721 (32) |
| H(1) | 0.332 (2) | 0.269 (2) | 0.390 (3) | 26 (6) | | | | | |
| H(2) | −0.027 (2) | 0.237 (2) | −0.422 (3) | 23 (5) | | | | | |
| H(3) | 0.269 (3) | −0.040 (2) | 0.849 (4) | 54 (9) | | | | | |
| H(4) | 0.146 (3) | −0.134 (2) | 0.756 (4) | 49 (9) | | | | | |
| H(5) | 0.307 (3) | −0.272 (3) | 0.617 (4) | 55 (9) | | | | | |
| H(6) | 0.357 (3) | −0.253 (2) | 0.844 (4) | 40 (7) | | | | | |
| H(7) | 0.434 (4) | −0.178 (3) | 0.755 (5) | 73 (14) | | | | | |
| H(8) | 0.397 (2) | 0.253 (2) | 0.712 (3) | 29 (6) | | | | | |
| H(9) | 0.395 (3) | 0.155 (2) | 0.842 (4) | 41 (8) | | | | | |
| H(10) | 0.626 (3) | 0.178 (3) | 0.828 (5) | 63 (10) | | | | | |
| H(11) | 0.563 (3) | 0.045 (2) | 0.753 (4) | 47 (9) | | | | | |
| H(12) | 0.567 (3) | 0.131 (3) | 0.598 (5) | 74 (12) | | | | | |
| H(13) | 0.460 (2) | 0.410 (2) | 0.250 (3) | 34 (5) | | | | | |
| H(14) | 0.417 (3) | 0.494 (3) | 0.117 (5) | 70 (12) | | | | | |
| H(15) | 0.244 (4) | 0.597 (3) | 0.225 (5) | 78 (11) | | | | | |
| H(16) | 0.295 (4) | 0.505 (4) | 0.402 (6) | 89 (15) | | | | | |
| H(17) | 0.408 (4) | 0.603 (4) | 0.384 (6) | 104 (14) | | | | | |
| H(18) | 0.266 (3) | 0.477 (3) | −0.207 (4) | 62 (10) | | | | | |
| H(19) | 0.153 (3) | 0.393 (3) | −0.365 (5) | 54 (11) | | | | | |
| H(20) | 0.074 (3) | 0.598 (3) | −0.303 (5) | 56 (9) | | | | | |
| H(21) | 0.097 (5) | 0.590 (4) | −0.085 (6) | 115 (18) | | | | | |
| H(22) | −0.026 (5) | 0.507 (4) | −0.245 (6) | 111 (16) | | | | | |

[a] In this and subsequent tables estimated standard deviations for the least significant figure are in parentheses. Parameters with no standard deviations were fixed by symmetry. The Debye–Waller factor is defined as: $T = \exp[-2\pi^2 \Sigma_i \Sigma_j a_i^* a_j^* h_i h_j U_{ij}]$. [b] The values for $U$ have been multiplied by $10^4$. For the hydrogen atoms, isotropic $B$'s defined by $\exp[-B(\sin^2 \theta)/\lambda^2]$ are given in the column labeled $U(11)$. These have been multiplied by 10.

Intensity data were collected on a Datex-Syntex automated four-circle diffractometer using Mo K$\alpha$ radiation ($\lambda$ 0.71069 Å). The radiation was monochromatized by pyrolytic graphite. The data were collected by the $\theta$–$2\theta$ scan method, monitoring the intensity scale by remeasuring a group of five standard reflections periodically. The intensities of these standard reflections varied by ±2% with no systematic trend, and no corrections were made. The scan rate was 1°/min. The scan range was 1.5°. Backgrounds at either end of the scan were collected for half the scan time. Independent reflections (3423) were measured out to a sin $\theta/\lambda$ of 0.65 or 27.5° in $\theta$. Of those independent reflections, 2080 reflections had a net intensity greater than $3\sigma_I$. This corresponds to a data/parameter ratio of 10.9 if hydrogen atoms are not included or 8.5 if they are included. The standard deviation $\sigma_I$ was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2(\text{count}) + K^2[S + B1 + B2]^2$, where $S$, $B1$, and $B2$ are the observed counts for the scan and two backgrounds, respectively. Ten reflections ranging in intensity from very strong to barely observed were measured at least 40 times each; then the value of $K$, which gave the best fit to the empirical standard deviation, was calculated. A value of 0.015 was used.

The intensities were corrected for coincidence using the method of Sletten, Sletten, and Jensen[5] ($\tau = 1.08 \times 10^{-7}$ count$^{-1}$). The

(5) E. Sletten, J. Sletten, and L. H. Jensen, *Acta Crystallogr., Sect. B*, 25, 1330, (1969).

small linear absorbtion coefficient ($\mu = 6.87$ cm$^{-1}$) indicated absorption effects could be neglected. Transmission coefficients range from 0.89 to 0.93. Structure factors were calculated in the normal way, assuming an ideally imperfect monochromator.

**Determination and Refinement of the Structure.** Because there is only one molecule in the unit cell of space group $P\bar{1}$, the nickel ion is required to be at a center of symmetry, selected to be the origin. The positions of the rest of the 21 nonhydrogen atoms in the asymmetric unit were easily found from a Fourier map with phases by the contributions from the nickel ion. The positions of the 22 hydrogen atoms in the asymmetric unit were located from a difference synthesis later in the refinement procedure.

Least-squares refinement using block diagonal and finally full-matrix methods was carried out. The function minimized was $\Sigma w(F_o - F_o)^2$, where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used, but in the final refinement all nonhydrogen atoms were refined assuming anisotropic thermal motion. The hydrogen atoms were assumed to have isotropic thermal motion. Because of computer memory limitations, the parameters had to be refined in two blocks during the full-matrix least-squares refinement. In one block all nonhydrogen atoms were refined. In the other block the nickel ion and the hydrogen atoms and the carbon atoms to which they are bonded were refined. The refinement converged with $R = \Sigma|F_o - |F_c||/\Sigma|F_o| = 0.045$ and $R_w$ $(\Sigma w|F_o - |F_c||^2/\Sigma w F_o^2)^{1/2} = 0.029$.

A correction for anomalous dispersion was made for the nickel

ion ($\Delta f' = 0.4$ to $0.3$, $\Delta f'' = 1.2$ to $1.0$).[6] Scattering factors were from the International Tables.[7] The nickel atom was assumed to be in the zero ionization state.

The data were examined by the method of Housty and Clastre.[8] No evidence of secondary extinction was found and no correction for this effect was made.

In the last cycle of refinement all shifts were less than one standard deviation with virtually all of the nonhydrogen atom parameters having a shift/error ratio less than 0.2. The final value of the standard deviation of an observation of unit weight was 1.50. A plot of $\Delta F/\sigma_F$ vs. $F_o$ showed very little variation with increasing $F_o$. In the final difference synthesis, no peak greater than 0.33 e/Å³ was found.

The following computer programs were used: LSLAT (least-squares cell parameter refinement), LINUS (modification of the Busing, Martin, and Levy ORFLS least-squares program),[9] ECSORTH (sorting and averaging of data), BDLR4 (block diagonal least-squares program), JIMDAP (version of the Zalkin–Fourier summation program), ORFFE (function and error program),[10] ORTEP (thermal ellipsoid plot program),[11] HOW (molecular geometry program), and NANOVA (analysis of variance of final residuals program of Hamilton and Snyder). Most of these are available in the Brookhaven National Laboratory computer library. In addition, several local data handling programs were used as well as the autoindexing and least-squares cell parameter refinement programs written in assembly language by Sparks[12] for the Data General NOVA computer. Extensive use was made of the interactive color TV raster display in this laboratory for which routines have been written by Sparks and extensively modified locally.[13,14]

The final positional and thermal parameters are given in Table II, while the root-mean-square components of thermal displacement along the principal axes of the thermal ellipsoids are given in Table III. A table of observed and calculated structure factors is available.[15]

## Discussion

The structure of 1,2,3,4,5,6,7,8-octaethylporphinato-nickel(II) as found in triclinic crystalline modification is shown in Figure 1. This figure also shows the number-ing system used. As in the tetragonal modification, the structure in the triclinic modification is a square-planar complex. Figures 2 and 3 are stereoviews of the structures of the triclinic and tetragonal forms, re-spectively. Figure 4 shows the average bond lengths and angles for both forms of NiOEP and also shows the nomenclature for the various types of carbon atoms which will be used in the subsequent discussion.

There are several differences in the structures found for the two crystalline forms. The two most striking are the differences in the Ni–N bond distances and the differences in the degree of planarity of the macrocycle.

The two Ni–N bond distances for the complex in the triclinic form are 1.959 (2) and 1.957 (2) Å. The N–Ni–N

(6) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p 215.

(7) D. T. Cromer, "International Tables for X-Ray Crystallography," Vol. IV, in press.

(8) J. Housty and J. Clastre, Acta Crystallogr., 10, 695 (1957).

(9) W. R. Busing, K. O. Martin, and H. Levy, ORFLS, A Fortran Crystallographic Least-Squares Program, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(10) W. R. Busing, K. O. Martin, and H. Levy, ORFFE, A Fortran Crystallographic Function and Error Program. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(11) C. K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-3794-Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(12) R. Sparks, "Computers in Chemistry and Industry," Vol. 5, Marcel Dekker, New York, N. Y., in press.

(13) T. V. Willoughby and E. F. Meyer, Jr., Abstracts, American Crystallography Association Winter Meeting, Gainesville, Fla., Paper F5.

(14) C. N. Morimoto and E. F. Meyer, Jr., Abstracts, American Crystallography Association Winter Meeting, Gainesville, Fla, Paper F6.

(15) See paragraph at end of paper regarding supplementary ma-terial.
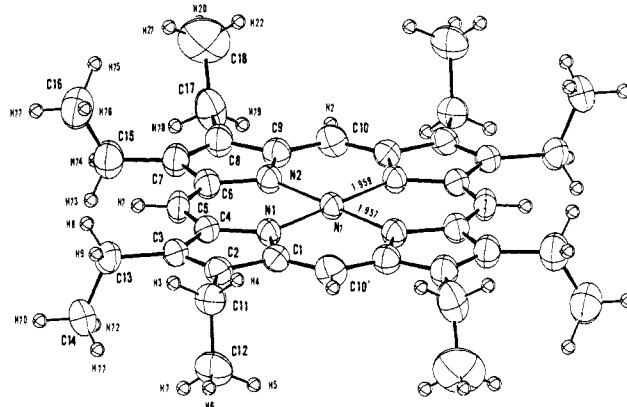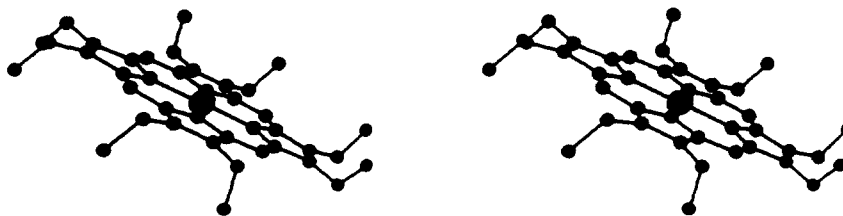
**Figure 1.** ORTEP drawing of the structure of 1,2,3,4,5,6,7,8-octaethylporphinatonickel(II) found in triclinic crystalline form. Numbering scheme and Ni–N bond distances are shown. Atoms not labeled are centrosymmetrically related. The thermal ellipsoids are drawn for 50% probability, except for those of the hydrogen atoms which are not drawn to scale.

**Table III.** Root-Mean-Square Amplitudes of Vibration (in Å) Along Principal Axes of Thermal Ellipsoids in Triclinic NiOEP

|       | Axis 1     | Axis 2     | Axis 3     |
|-------|------------|------------|------------|
| Ni    | 0.167 (1)  | 0.185 (1)  | 0.214 (1)  |
| N(1)  | 0.161 (5)  | 0.183 (4)  | 0.219 (4)  |
| N(2)  | 0.172 (5)  | 0.189 (4)  | 0.223 (4)  |
| C(1)  | 0.184 (5)  | 0.201 (5)  | 0.213 (5)  |
| C(2)  | 0.176 (5)  | 0.205 (5)  | 0.228 (5)  |
| C(3)  | 0.172 (5)  | 0.196 (5)  | 0.239 (5)  |
| C(4)  | 0.174 (5)  | 0.187 (5)  | 0.232 (5)  |
| C(5)  | 0.159 (5)  | 0.214 (5)  | 0.268 (5)  |
| C(6)  | 0.184 (5)  | 0.200 (5)  | 0.238 (5)  |
| C(7)  | 0.184 (5)  | 0.208 (5)  | 0.259 (5)  |
| C(8)  | 0.190 (5)  | 0.207 (5)  | 0.250 (5)  |
| C(9)  | 0.192 (5)  | 0.204 (5)  | 0.219 (5)  |
| C(10) | 0.166 (6)  | 0.221 (5)  | 0.248 (5)  |
| C(11) | 0.191 (5)  | 0.229 (5)  | 0.251 (5)  |
| C(12) | 0.183 (6)  | 0.272 (6)  | 0.284 (5)  |
| C(13) | 0.174 (5)  | 0.228 (5)  | 0.272 (5)  |
| C(14) | 0.187 (5)  | 0.267 (5)  | 0.282 (5)  |
| C(15) | 0.208 (5)  | 0.238 (6)  | 0.286 (6)  |
| C(16) | 0.220 (5)  | 0.287 (5)  | 0.332 (6)  |
| C(17) | 0.198 (6)  | 0.221 (6)  | 0.324 (6)  |
| C(18) | 0.198 (6)  | 0.297 (6)  | 0.408 (6)  |

bond angle is 90.15 (9)°. The Ni–N bond lengths in this form are significantly longer than the bond length of 1.929 (3) Å found in the tetragonal form. The bond length in the tetragonal form is the shortest yet found for a metalloporphyrin.

Perhaps the most remarkable feature about the tetragonal form of NiOEP is the marked nonplanarity of the macrocycle. There is a $S_4$ ruffling of the por-phinato core such that the angle between planes of adjacent pyrrole rings is 32.8°. In contrast, the com-plex is centrosymmetric and is reasonably planar in the triclinic form of NiOEP with the angle between planes of adjacent pyrrole rings being 2.1°. Most so-called planar porphyrins have angles between adjacent pyrrole groups in the range of 3–5°. Table IV gives the deviations from a number of least-squares planes in the triclinic form. The largest deviation from the plane defined by the entire macrocycle for the triclinic form is 0.02 Å. In contrast, the methine carbon atoms in the tetragonal form lie 0.51 Å out of the least-squares plane defined by the nickel ion and four pyrrole nitrogen atoms.

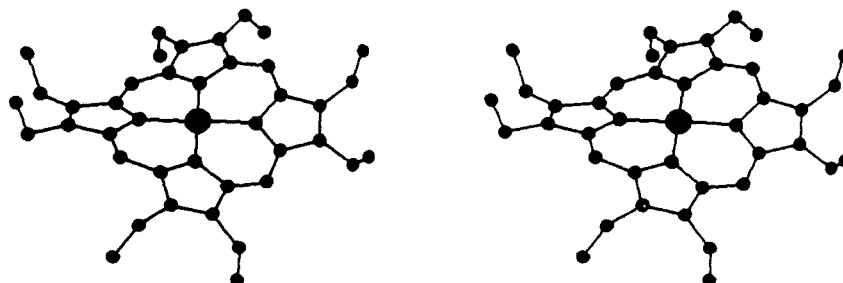**Figure 2.** Stereoview of triclinic NiOEP.



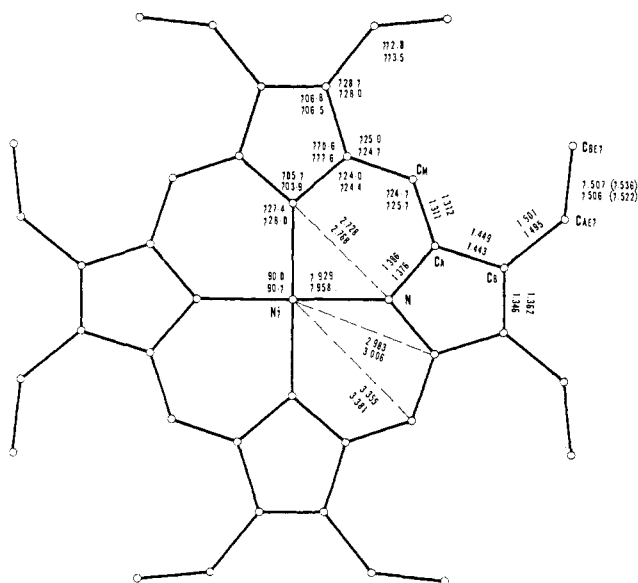**Figure 3.** Stereoview of tetragonal NiOEP.



**Figure 4.** Schematic drawing of NiOEP showing averaged bond lengths in ångströms and angles in degrees for the triclinic (lower value) and tetragonal (upper value) forms. The values in parentheses are the distances corrected for thermal motion. Also shown is the notation for different types of carbon atoms.

**Table IV.** Deviation (Å) from Least-Squares Planes for Triclinic NiOEP[a]

|  | Plane 1 | Plane 2 | Plane 3 | Plane 4 |
|---|---|---|---|---|
| Ni | −0.016 | 0.000 | 0.031 | −0.046 |
| N(1) | −0.011 | 0.000 | 0.006 | −0.007 |
| N(2) | 0.014 | 0.000 | 0.051 | 0.002 |
| C(1) | −0.016 | 0.009 | −0.007 | −0.008 |
| C(2) | 0.019 | 0.034 | 0.005 | 0.054 |
| C(3) | 0.021 | 0.015 | −0.001 | 0.069 |
| C(4) | −0.001 | −0.009 | −0.003 | 0.027 |
| C(5) | −0.011 | −0.039 | −0.015 | 0.021 |
| C(6) | −0.014 | −0.045 | 0.001 | −0.001 |
| C(7) | −0.020 | −0.071 | −0.006 | −0.001 |
| C(8) | 0.006 | −0.041 | 0.041 | 0.002 |
| C(9) | 0.021 | −0.004 | 0.070 | −0.002 |
| C(10) | 0.008 | −0.007 | 0.080 | −0.042 |
| C(11) | 0.011 | 0.037 | −0.017 | 0.058 |
| C(13) | −0.006 | −0.030 | −0.053 | 0.069 |
| C(15) | −0.081 | −0.153 | −0.090 | −0.037 |
| C(17) | 0.057 | −0.005 | 0.101 | 0.048 |

Plane 1, Macrocycle (Ni, N(1), N(2), C(1)–C(10))
$-8.36X + 5.32Y + 3.49Z = 0.016$

Plane 2, Ni, N(1), N(2)
$-8.44X + 5.18Y + 3.51Z = 0.00$

Plane 3, Pyrrole ring 1. (N(1), C(1)–C(4))
$-8.42X + 5.29Y + 3.41Z = -0.032$

Plane 4, Pyrrole ring 2. (N(2), C(6)–C(9))
$-8.27X + 5.38Y + 3.58Z = 0.046$

[a] All planes are unweighted. $X$, $Y$, and $Z$ are in triclinic fractional coordinates.

The normal radius of the "hole" in an undistorted metalloporphyrin has been estimated to be 2.01 Å.[16] On the other hand normal Ni–N bond lengths in square-planar complexes are *ca.* 1.85 Å.[17] Thus to accommodate an undersized ion like low spin Ni(II), the porphinato core must contract. Hoard[2] provided a detailed treatment of the correlation between the size of the metal ion and the degree of planarity in the porphyrin. He had postulated that 1.96 Å is the smallest radius the "hole" in a porphyrin may have and still retain a planar macrocycle. If the radius of the "hole" is to become smaller than 1.96 Å, the porphinato core must distort from planarity, presumably to an ef-

fectively $D_{2d}$ symmetry as was found in the tetragonal form of NiOEP. The present work seems to confirm Hoard's theory as the average Ni–N bond length of 1.958 (2) Å in triclinic NiOEP agrees well with the values of 1.96 (1) Å found in nickel(II) 2,4-diacetyl-deuteroporphyrin IX dimethyl ester (NiDEUT)[18] and 1.957 (13) Å found in nickel(II) etioporphyrin I.[19] These latter two compounds are both effectively planar. The angles between adjacent pyrrole rings in NiDEUT range from 1.9 to 5.2°.

There are also some significant differences in the bond

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(17) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(18) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 2305 (1965).

(19) E. B. Fleischer, *J. Amer. Chem. Soc.*, **85**, 146 (1963).

**Table V.** Bond Lengths and Angles for Triclinic NiOEP[b]

| | Bond lengths | Bond angles | |
|---|---|---|---|
| Ni–N(1) | 1.959 (2) | N(1)–Ni–N(2) | 90.15 (9) |
| Ni–N(2) | 1.957 (2) | Ni–N(1)–C(1) | 128.2 (2) |
| N(1)–C(1) | 1.367 (4) | Ni–N(1)–C(4) | 127.7 (2) |
| N(1)–C(4) | 1.380 (4) | Ni–N(2)–C(6) | 128.0 (2) |
| N(2)–C(6) | 1.376 (4) | Ni–N(2)–C(9) | 128.2 (2) |
| N(2)–C(9) | 1.379 (4) | C(1)–N(1)–C(4) | 104.2 (2) |
| C(1)–C(2) | 1.444 (4) | C(6)–N(2)–C(9) | 103.7 (2) |
| C(1)–C(10)'[a] | 1.369 (4) | N(1)–C(1)–C(2) | 111.9 (3) |
| C(2)–C(3) | 1.348 (4) | N(1)–C(1)–C(10)'[a] | 124.7 (3) |
| C(2)–C(11) | 1.490 (4) | C(2)–C(1)–C(10)'[a] | 123.5 (3) |
| C(3)–C(4) | 1.447 (4) | C(1)–C(2)–C(3) | 106.2 (3) |
| C(3)–C(13) | 1.499 (4) | C(1)–C(2)–C(11) | 125.5 (3) |
| C(4)–C(5) | 1.367 (4) | C(3)–C(2)–C(11) | 128.3 (3) |
| C(5)–C(6) | 1.375 (4) | | |
| C(6)–C(7) | 1.439 (4) | C(2)–C(3)–C(4) | 106.7 (3) |
| C(7)–C(8) | 1.344 (4) | C(2)–C(3)–C(13) | 128.2 (3) |
| C(7)–C(15) | 1.503 (5) | C(4)–C(3)–C(13) | 125.1 (3) |
| C(8)–C(9) | 1.445 (4) | C(3)–C(4)–C(5) | 124.3 (3) |
| C(8)–C(17) | 1.489 (5) | N(1)–C(4)–C(3) | 111.1 (3) |
| C(9)–C(10) | 1.375 (4) | N(1)–C(4)–C(5) | 124.6 (3) |
| C(11)–C(12) | 1.514 (4) | C(4)–C(5)–C(6) | 125.3 (3) |
| | 1.524 (5)[c] | N(2)–C(6)–C(5) | 124.2 (3) |
| C(13)–C(14) | 1.519 (5) | N(2)–C(6)–C(7) | 111.6 (3) |
| | 1.530 (5)[c] | C(5)–C(6)–C(7) | 124.2 (3) |
| C(15)–C(16) | 1.486 (6) | C(6)–C(7)–C(8) | 106.9 (3) |
| | 1.501 (6)[c] | C(6)–C(7)–C(15) | 125.6 (3) |
| C(17)–C(18) | 1.502 (6) | C(8)–C(7)–C(15) | 127.5 (3) |
| | 1.534 (6)[c] | C(7)–C(8)–C(9) | 106.2 (3) |
| Ni–C(5) | 3.380 (3) | C(7)–C(8)–C(17) | 128.2 (3) |
| Ni–C(10) | 3.382 (3) | C(9)–C(8)–C(17) | 125.6 (3) |
| N(1)–N(2) | 2.772 (3) | N(2)–C(9)–C(8) | 111.6 (3) |
| N(1)–N(2)'[a] | 2.765 (3) | N(2)–C(9)–C(10) | 124.0 (3) |
| Ni–C(1) | 3.002 (3) | C(8)–C(9)–C(10) | 124.4 (3) |
| Ni–C(4) | 3.007 (3) | C(9)–C(10)–C(1)'[a] | 125.1 (3) |
| Ni–C(6) | 3.007 (3) | C(2)–C(11)–C(12) | 113.6 (3) |
| Ni–C(9) | 3.012 (3) | C(3)–C(13)–C(14) | 113.6 (3) |
| N(1)–N(2) | 2.772 (3) | C(7)–C(15)–C(16) | 113.7 (4) |
| N(1)–N(2)'[a] | 2.765 (3) | C(8)–C(17)–C(18) | 113.3 (4) |

[a] Primed atoms related to unprimed by symmetry operation X' = –X, Y' = –Y, Z' = –Z. [b] Some nonbonding distances of interest are also given. [c] Corrected for thermal motion.

DEUT.[18] The average bond lengths and angles for three other compounds are included in Table VI. One of these compounds, $\alpha,\beta,\gamma,\delta$-tetrapropylporphinatocopper(II)[4] (CuTPrP), is a square-planar complex with an average M–N distance of 2.00 Å, which is a nearly optimal value for undistorted accommodation within the central porphine core. The other complex is octaethylporphinatodichlorotin(IV) (Cl₂SnOEP)[20] in which an oversize metal ion is bonded causing an unusually long M–N distance for metalloporphyrins, 2.081 (2) Å, and thus an *expansion* of the porphine core in contrast to the situation with NiOEP in which there is a *contraction* of the core. The third compound is the free base of octaethylporphyrin.[3]

Within experimental error, there do not appear to be any significant trends in the bond lengths except for the M–$C_m$ and N–N distances which increase as the radius of the central hole increases. It will be noted that the longest M–$C_m$ distance is found in CuTPrP which unlike the other compounds in Table VI is substituted at the meso carbon atom positions. This lengthening is an effect that has been observed for several other meso-substituted porphyrins[20] when they are compared with analogous $\beta$-carbon substituted porphyrins. As a result of the longer M–$C_m$ distance, the bond angles around $C_a$ and $C_m$ in CuTPrP also do not fit the trend observed for the other compounds in Table VI.

There are some interesting trends in the bond angles, particularly the $C_a$–N–$C_a$ and N–$C_a$–$C_b$ angles. The former decreases for the planar configurations, then increases for the ruffled configuration found for the tetragonal form of NiOEP. The latter angle increases with decreasing M–N distances for the planar configuration then decreases for tetragonal NiOEP. Hoard[2] has noted this tendency and points out that an increase in the $C_a$–N–$C_a$ angle is conducive to stronger complexing, but the amount of expansion of this angle

**Table VI.** Averaged Bond Lengths (Å) and Angles (deg) of Various Porphyrins and Metalloporphyrins[i]

| | Tetragonal[a] NiOEP | Triclinic[b] NiOEP | NiDEUT[c] | CuTPrP[d] | Cl₂SNOEP[e] | H₂OEP[f,g] Ring(1) | H₂OEP[f,g] Ring(2)[h] |
|---|---|---|---|---|---|---|---|
| M–N | 1.929 (3) | 1.958 (2) | 1.960 (14) | 2.000 (5) | 2.082 (2) | 2.026 (2) | 2.098 (2) |
| $C_a$–N | 1.386 (2) | 1.376 (6) | 1.382 (19) | 1.381 (10) | 1.379 (5) | 1.363 (1) | 1.367 (1) |
| $C_a$–$C_m$ | 1.372 (2) | 1.371 (4) | 1.374 (25) | 1.389 (4) | 1.386 (10) | 1.392 (3) | |
| $C_a$–$C_b$ | 1.449 (5) | 1.443 (3) | 1.447 (15) | 1.448 (1) | 1.437 (12) | 1.462 (2) | 1.437 (2) |
| $C_b$–$C_b$ | 1.362 (5) | 1.346 (2) | 1.350 (19) | 1.344 (1) | 1.368 (5) | 1.354 (2) | 1.373 (2) |
| M–$C_m$ | 3.355 (4) | 3.381 (1) | 3.403 (13) | 3.444 (1) | 3.424 (10) | 3.422 (2) | |
| M–$C_a$ | 2.983 (1) | 3.006 (4) | 3.011 (21) | 3.035 (6) | 3.099 (4) | 3.050 (1) | 3.094 (1) |
| N–N | 2.728 (4) | 2.768 (5) | 2.772 (17) | 2.828 (2) | 2.994 (2) | 2.916 (1) | 2.826 (2) |
| N–M–N | 90.0 | 90.15 (9) | 90.0 (6) | 90.3 (5) | 90.0 (1) | | |
| M–N–$C_a$ | 127.4 (2) | 128.0 (2) | 127.8 (6) | 126.9 (3) | 125.9 (4) | | |
| $C_a$–N–$C_a$ | 105.1 (3) | 103.9 (4) | 104.5 (6) | 106.2 (4) | 108.2 (2) | 105.7 (2) | 109.6 (2) |
| N–$C_a$–$C_m$ | 124.0 (2) | 124.4 (3) | 125.3 (13) | 126.7 (1) | 124.4 (4) | 125.1 (2) | 125.0 (2) |
| N–$C_a$–$C_b$ | 110.6 (2) | 111.6 (3) | 111.0 (8) | 109.5 (6) | 108.3 (7) | 110.8 (1) | 107.7 (2) |
| $C_b$–$C_a$–$C_m$ | 125.0 (2) | 124.1 (4) | 123.7 (18) | 123.8 (6) | 127.3 (4) | 124.0 (1) | 127.3 (1) |
| $C_a$–$C_m$–$C_a$ | 124.1 (2) | 125.1 (1) | 123.9 (13) | 122.8 (1) | 129.5 (4) | 127.6 (3) | |
| $C_a$–$C_b$–$C_b$ | 106.8 (3) | 106.5 (4) | 106.8 (10) | 107.3 (4) | 107.6 (3) | 106.3 (1) | 107.5 (2) |

[a] Reference 1. [b] This work. [c] Reference 18. [d] Reference 4. [e] Reference 20. [f] Reference 3. [g] For H₂OEP, M refers to center of macrocycle. [h] Ring which contains the imino-hydrogen atom. [i] Figures in parentheses are the rms standard deviation of the average, when there is more than one contribution to the average. Otherwise, the esd is given.

lengths and angles found for the macrocycle in the two forms. Table V summarizes the bond lengths and angles for the triclinic form while Table VI gives the averaged bond lengths and angles and compares them with those found in the tetragonal form and in Ni-

is limited by the need to keep the N–$C_a$–$C_b$ angle as large as possible.

Moustakali and Tulinsky[4] have compared the

(20) D. L. Cullen and E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **29**, 2507 (1973).
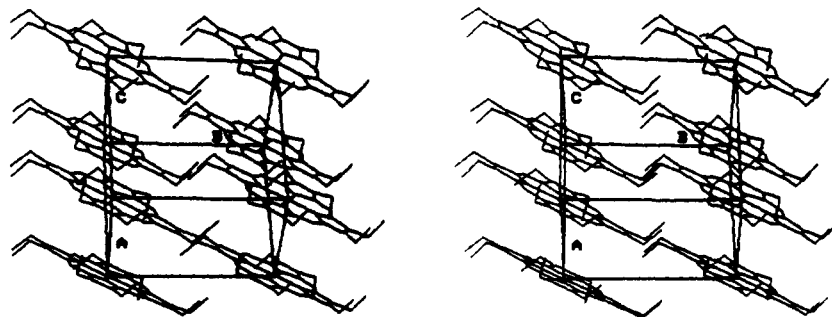
Figure 5.  Stereoview of packing in the unit cell for the triclinic form of  NiOEP.
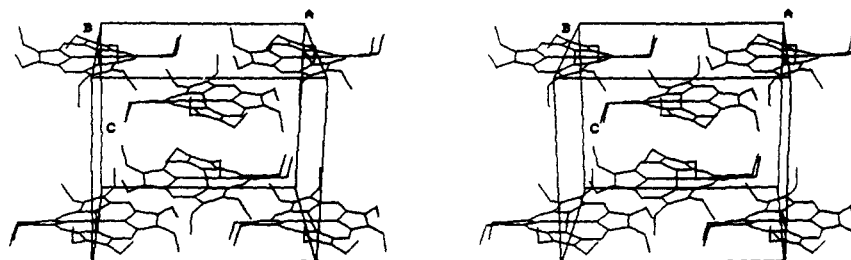
Figure 6.  Stereoview of packing in the unit cell for the tetragonal form of NiOEP.

structures of CuTPrP and the analogous free base, H₂TPrP. These two compounds are isomorphous. The effect of metal substitution is to cause a general "squaring up" and overall contraction of the central core region. Similar observations can be made for triclinic NiOEP and the isomorphous structure of free base, H₂OEP. Because of the smaller metal ion, the contraction is even more pronounced. There is good agreement between the averaged bond length and angles in CuTPrP and in the azo–pyrrole ring of the free base.[4]  However, the agreement is not as good when NiOEP and H₂OEP are compared, because of the changes in the bond parameters in NiOEP needed to accommodate the severely contracted porphinato core.

The values for the terminal C–C bonds as originally calculated are unusually short.  This is probably due to thermal shortening.  When these bond distances were corrected for thermal motion assuming a "riding" model, more reasonable values were obtained.  Both values are given in Table V.

The two C–H bond lengths involving sp² carbons are 0.89 (2) and 0.90 (2) Å for C(5)–H(1) and C(10)–H(2), respectively.  The average C–C–H bond angle around C(5) and C(10) is 117 (4)°.  The C–H bond lengths for the ethyl groups range from 0.86 to 1.12 Å.  Bond angles vary from 106.8 to 115.3° for C–C–H angles, and from 92.4 to 112.3° for H–C–H angles.  The estimated standard deviation for C–H bonds in the ethyl groups is 0.02–0.04 Å, for C–C–H angles it is 1.5–2.5°, and for H–C–N angles it is 2.5–3.5°.  The hydrogen atoms of the ethyl groups show the expected staggered configuration.

This is the first example of the same pure metalloporphyrin being found in two crystalline modifications with quite different configurations of the macrocycle.  However, the structure of the free base of α,β,γ,δ-tetraphenylporphine (H₂TPP) has been determined in two crystalline modifications.  Like NiOEP, the tri-

clinic form is approximately planar[21] while the tetragonal form has a severe ruffling of the macrocycle.[22] A third unstable orthorhombic form has been reported.[23] The square-planar complexes of copper(II) and palladium(II) with tetraphenylporphine (CuTPP and PdTPP) are isomorphous with the tetragonal form of the free base.[24]  CuTPrP and its free base are also isomorphous, both crystallizing in a monoclinic space group and both being approximately planar.[4,25]

From these results it is apparent that the energies involved in deforming the porphyrin molecule are not large.  In the case of NiOEP one reason postulated for the deformation is to decrease the Ni–N bond length.  Obviously this is not a factor in the two forms of tetraphenylporphine or in the two copper complexes.  Packing forces may be the determining factor as to which form is obtained in the crystalline state.

In neither of the two forms of NiOEP are there any unusually short intermolecular contacts.  The shortest intermolecular contacts between nonhydrogen atoms is 3.50 Å for the triclinic form and 3.53 Å for the tetragonal form.  Figures 5 and 6 show stereoviews of the packing in the triclinic and tetragonal forms, respectively.

To evaluate semiquantitatively the effect of packing forces, use was made of the PCK5 program of Williams,[26] which approximates the interatomic nonbonded repulsive potential energy, $\epsilon_R(i,j)$, of a pair of atoms $(i,j)$ such that the following equations hold.

$$\epsilon_R = w_p(d_0 - d_{ij})^2 \qquad d_{ij} \leq d_0$$
$$\epsilon_R = 0 \qquad d_{ij} > d_0$$

(21) S. Silvers and A. Tulinsky, J. Amer. Chem. Soc., 89, 3331 (1967).

(22) M. J. Hamor, T. A. Hamor, and J. L. Hoard, J. Amer. Chem. Soc., 86, 1938 (1964).

(23) E. B. Fleischer, Accounts Chem. Res., 3, 105 (1969).

(24) E. B. Fleischer, C. Miller, and L. Webb, J. Amer. Chem. Soc., 86, 2342 (1964).

(25) P. W. Codding and A. Tulinsky, J. Amer. Chem. Soc., 94, 4151 (1972).

(26) D. E. Williams, Acta Crystallogr., Sect. A, 25, 464 (1969).

The interatomic distance is $d_{ij}$, $d_0$ is an empirical cutoff distance, and $w_p$ is a weighting factor. The total repulsive energy, $E_R$, can be calculated by summing over all pairwise energies, $\epsilon_R$. The program searches for a position of minimum energy with the help of least-squares procedures. As has been pointed out by Zugenmaier and Sarko,[27] who have recently done packing studies on a series of monosaccharides, the absolute magnitude of $E_R$ is probably relative, but a consideration of the differences in energies for similar compounds is meaningful.

Such an assumption should also hold true when different packing arrangements of the same compounds are considered. For this reason packing calculations were carried out on the two forms of NiOEP[1] and on the two forms of tetraphenylporphine.[21,22] For comparison the calculations were also performed on the copper and palladium tetraphenylporphine complexes,[24] the free base of tetra-$n$-propylporphine and its copper complex,[4,25] and the free base of octaethylporphyrin. In each case the structure as determined from the X-ray diffraction studies was used as the starting position and refined to obtain the structure with the minimum $E_R$ value. The macrocycle was treated as a rigid group in these refinements. Since in every case the center of gravity of the molecule is fixed by symmetry, no translation is allowed and only rotational parameters need be considered. In the case of the molecules in tetragonal space groups, the only rotation allowed is about the $z$ direction. The interaction parameter sets used are listed in Table VII.

**Table VII.** Parameter Set for Packing Analysis[a]

| | Set 1 | | | Set 2 | |
|---|---|---|---|---|---|
| | $w_p$ | $d_0$ | | $w_p$ | $d_0$ |
| CH₃–CH₃ | 1.00 | 4.60 | C–C | 1.87 | 3.65 |
| CH₃–N | 1.00 | 4.00 | N–N | 1.87 | 3.65 |
| CH₃–C | 1.00 | 4.00 | C–N | 1.87 | 3.65 |
| N–N | 1.00 | 3.60 | C–H | 1.56 | 3.03 |
| N–C | 1.00 | 3.60 | N–H | 1.56 | 3.03 |
| C–C | 1.00 | 3.60 | H–H | 1.00 | 2.88 |

[a] $w_p$ has units kcal mol⁻¹ Å⁻², $d_0$ has units of Å.

Three cases were assumed for the model and potential parameters. (1) Hydrogen atoms were neglected. Instead each of the alkyl carbon atoms was treated as a spherical methyl group and given a large $d_0$ value. The potential set 1 as listed in Table VII was used. Calculations were not carried out on tetraphenylporphine or its complexes. (2) The positions of the hydrogen atoms were calculated assuming a C–H bond length of 1.0 Å. For the alkyl groups, an ideally staggered configuration was assumed. Potential set 2 in Table VII was used. This set of potential parameters uses the values listed by Williams.[26] (3) With the exceptions of tetraphenylporphine (tetragonal form) and octaethylporphyrin, observed hydrogen atom positions were used along with potential set 2. No hydrogen atom positions were given for the former compound while for the latter only "idealized" hydrogen atom positions were given.

For the purposes of the calculations in the case of the

metalloporphyrins, the metal ion potential was approximated to be the same as that for carbon atoms. Since, for each of the three types of porphyrins considered, there is a free base structure which is isomorphous with one form of its square-planar metal complex, it is apparent that interactions involving the metal ion have little effect on the packing, a conclusion which was verified by the calculations.

The results are summarized in Table VIII. The measure of the average deviation between actual and predicted coordinates,[27] $\phi$, is defined as

$$\phi = \left( \sum_{i=1}^{N} \Delta_i^2 / 3N \right)^{1/2}$$

where $N$ is the number of atoms in the molecule and $\Delta_i$ is the difference between corresponding atom positions in the predicted and actual structure. From the values given in Table VIII, it is seen that in virtually every case there were only small deviations from the starting structure.

The results of the calculations are less conclusive than hoped. The major difficulty is that the major contributions to the packing energy come from H···H interactions, and it is an inherent problem with X-ray data that hydrogen positions are relatively inaccurate. This problem is compounded for several of the cases in Table VIII, particularly for tetraphenylporphine and its complexes, since the structures were determined in different laboratories with differing degrees of accuracy. However, in the case of NiOEP, the standard deviations of the hydrogen atom positions are approximately the same in the two forms.

Because of the uncertainties, no conclusions can be made about the two forms of tetraphenylporphine, since the relative energies change depending on the assumption used. However, for NiOEP, the $E_R$ for the tetragonal form is considerably less than for the triclinic form in all three cases. It should also be noted that the volume/molecule ratio is approximately the same in the two forms of H₂TPP, but the triclinic form of NiOEP has a significantly smaller volume/molecule ratio than the tetragonal form.

It has been suggested[2] that the planar form would be favored in an unconstrained environment, and this is probably the case for the free base of tetraphenylporphine, although the energy difference must be small. In NiOEP where the difference in packing energies is larger, the indication is that the ruffled form would be more favored in an unconstrained environment, at least in noncoordinating solvents. It would seem that the shortening of the Ni–N bond lengths toward more normal values compensates at least partially for the loss of energy due to partial destruction of the $\pi$-conjugation system. Because of the packing forces, the planar triclinic form is not as free to distort as the tetragonal form of NiOEP. However, as has been pointed out, the results leading to this conclusion are not conclusive, and it may be that other factors, such as thermodynamic considerations, may also play an important part in determining whether the planar or ruffled form is favored in an unconstrained environment.

Thermodynamic studies[28] have shown that in

(27) P. Zugenmaier and A. Sarko, *Acta Crystallogr., Sect. B*, **28**, 3158 (1972).

(28) S. J. Cole, G. C. Curthoys, E. A. Magnuson, and J. N. Phillips, *Inorg. Chem.*, 11, 1024 (1972).

**Table VIII.** Summary of Packing Energy Calculations[b]

| | Space group | Vol/molecule ($Å^3$) | Interplanar angle between adjacent pyrrole rings (deg) | Case[a] | $E_R$(kcal/mol), initial | $E_R$(kcal/mol), final | $\phi$, Å |
|---|---|---|---|---|---|---|---|
| | | | A. Octaethylporphyrins (OEP) | | | | |
| $H_2OEP*$ | $P\bar{1}$ | 745 | 3.1 | 1 | 18.12 | 17.67 | 0.004 |
| | | | | 2 | 2.84 | 2.63 | 0.016 |
| NiOEP(Tri*) | $P\bar{1}$ | 743 | 2.1 | 1 | 17.59 | 17.20 | 0.008 |
| | | | | 2 | 3.26 | 2.84 | 0.026 |
| | | | | 3 | 1.99 | 1.77 | 0.012 |
| NiOEP(Tet) | $I4_1/a$ | 771 | 32.8 | 1 | 11.30 | 11.12 | 0.001 |
| | | | | 2 | 1.53 | 1.38 | 0.001 |
| | | | | 3 | 1.52 | 1.38 | 0.001 |
| | | | B. Tetraphenylporphyrins (TPP) | | | | |
| $H_2TPP$(Tri) | $P\bar{1}$ | 799 | 7.4 | 2 | 3.27 | 2.68 | 0.041 |
| | | | | 3 | 3.75 | 3.17 | 0.041 |
| $H_2TPP$(Tet*) | $I\bar{4}2d$ | 797 | 23.8 | 2 | 3.15 | 3.12 | 0.001 |
| CuTPP* | $I\bar{4}2d$ | 791 | 26.8 | 2 | 3.95 | 3.95 | 0.001 |
| | | | | 3 | 4.03 | 3.86 | 0.001 |
| PdTPP* | $I\bar{4}2d$ | 796 | 25.2 | 2 | 2.81 | 2.80 | 0.001 |
| | | | | 3 | 4.14 | 4.11 | 0.001 |
| | | | C. Tetrapropylporphyrins (TPrP) | | | | |
| $H_2TPrP*$ | $P2_1/c$ | 650 | 4.5 | 1 | 8.52 | 7.23 | 0.129 |
| | | | | 2 | 3.25 | 2.17 | 0.061 |
| | | | | 3 | 3.00 | 2.79 | 0.020 |
| CuTPrP* | $P2_1/c$ | 642 | 3.7 | 1 | 9.35 | 8.02 | 0.127 |
| | | | | 2 | 3.91 | 2.50 | 0.063 |
| | | | | 3 | 3.58 | 3.20 | 0.033 |

[a] See text for details. [b] Asterisk denotes compounds of each type which are isomorphous.

solution 1:1 pyridine adducts are probably formed with nickel(II) porphyrin. The possibility of 2:1 complexes is far less likely. However, the $\Delta G°$ for monoadduct formation, though favorable, is small, indicating that the tendency toward adduct formation is weak. This conclusion was further supported by the current study in which a square-planar complex was crystallized from a solution with a high concentration of pyridine.

In an attempt to elucidate the configuration of the macrocycle in solution, some nmr studies on NiOEP were carried out. Samples were dissolved in deuterio-chloroform and proton magnetic resonance spectra were taken on a Varian Associates HA100 spectrometer, both with and without pyridine added to the solution. The results were inconclusive. There was no observed shift in the peak due to methine hydrogen atoms relative to the methylene hydrogen atom peaks. However, since the energy difference between the ruffled and planar forms is probably small, it may be, as has been suggested,[2] that there is a rapid reflection of conformation through the equatorial plane, which would make a distinction impossible to detect, at least at room temperature. The limited solubility of NiOEP in deuteriochloroform discouraged further studies at lower temperatures.

In previous studies[28] small shifts in the nmr peaks due to the pyridine hydrogen atoms were observed when pyridine was added to nickel(II) porphyrin solutions. No such shifts were observed in this work.