

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1965, by the American Chemical Society

VOLUME 87, NUMBER 11

JUNE 5, 1965

Physical and Inorganic Chemistry

The Crystal and Molecular Structure of Nickel(II) 2,4-Diacetyldeuteroporphyrin-IX Dimethyl Ester¹

T. A. Hamor,² W. S. Caughey,³ and J. L. Hoard^{2,4}

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York, and the Department of Physiological Chemistry, The Johns Hopkins School of Medicine, Baltimore, Maryland. Received January 21, 1965

A quantitative stereochemical description of the nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester molecule is obtained from a three-dimensional X-ray analysis of the crystalline structure. The unit cell of the triclinic crystal contains two molecules of the porphyrin and one of benzene as solvent of crystallization; the space group is $P\bar{1}$. The more important results bear directly upon the adaptability of the rather flexible porphine skeleton to a considerable range of stereochemical requirements. Comparison of analogous porphyrin and phthalocyanine structures reveals both interesting parallels and significant differences.

Introduction

As recently as 1962, when the study of nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester to be described herein was undertaken along with that already reported^{5,6} for tetraphenylporphine, the porphine skeleton was commonly assumed to be planar. The plausibility of this assumption was supported, albeit less directly than was generally recognized, by the crystal structure data obtained for the chemically related phthalocyanines by Robertson, *et al.*,⁷ and by

noting that a planar configuration would be favored by a sufficiently general delocalization of the π -bonding. It seems to have gone unremarked that, unlike the case of an aromatic hydrocarbon, angular strain in the pattern of σ -bonding probably cannot be minimized in a strictly planar porphine skeleton and that, with σ - and π -bonding in some degree working at cross-purposes, the porphine skeleton—whether or not it be planar in the unconstrained state—should be quite easily deformable normal to its mean plane.^{5,6}

Meaningful determinations of crystalline structure and molecular stereochemistry for porphyrins, achieved in every case by the analysis of three-dimensional X-ray diffraction data from single crystals, began to appear during 1963. A particularly marked ruffling of the porphine skeleton, taken in agreement with a fourfold axis of rotary inversion, characterizes molecules of the copper(II),^{8,9} palladium(II),⁹ and metal-free^{5,6} tetraphenylporphines as these exist in the isomorphous series of tetragonal crystals. Significantly nonplanar porphine skeletons are observed also in crystals of nickel(II) etioporphyrin-I,¹⁰ of a triclinic tetraphenylporphine,¹¹ and of chlorohemin.¹² During study of tetragonal tetraphenylporphine, however, it was noted that the pattern of thermal motions of the atom was that expected for highly anisotropic deformability of the porphine skeleton (*vide supra*); consequently, it

(1) Support of this work by the National Institutes of Health of the Public Health Service, the National Science Foundation, and the Advanced Research Projects Agency is gratefully acknowledged. We also thank the Cornell Computing Center, John W. Rudan, Director.

(2) Department of Chemistry, Cornell University, Ithaca, N. Y.

(3) Department of Physiological Chemistry, The Johns Hopkins University, Baltimore, Md.

(4) Author to whom correspondence should be addressed.

(5) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Am. Chem. Soc.*, **85**, 2334 (1963).

(6) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

(7) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 236 (1940).

(8) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 1353 (1963).

(9) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

(10) E. B. Fleischer, *ibid.*, **85**, 146 (1963).

(11) S. Silvers and A. Tulinsky, *ibid.*, **86**, 927 (1964).

(12) D. F. Koenig, *Acta Cryst.*, in press.

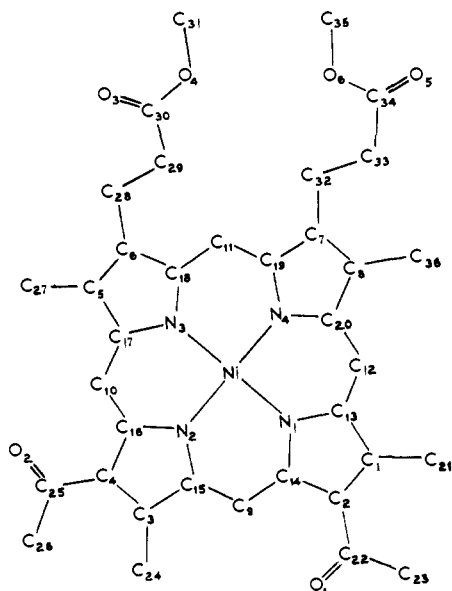


Figure 1. Skeletal diagram of the nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester (abbreviated as NiDeut—see Table II) molecule. Atoms are numbered in agreement with Tables I, II, and VI.

was suggested that, given the appropriate environment, the skeleton could closely simulate or attain planarity.^{5,6} Although these expectations seem to be realized in the recently published structures⁹ for diaquozinc(II) tetraphenylporphine and aquohydroxyiron(III) tetraphenylporphine, both studies carry some puzzling features which, we surmise, might have their origins in molecular packing disorders—phenomena which are all too common in porphyrin crystals. Inasmuch as these unexpected features center upon the apparently six-coordinate metal atoms and their immediate neighbors, the matter is discussed further in the accompanying report¹³ on the structure of crystalline methoxyiron(III) mesoporphyrin-IX dimethyl ester. The porphine skeleton in this mesoporphyrin molecule is slightly convex, and the iron(III) atom, as in chlorohemin,¹² is quite definitely five-coordinate.

Further evidence of the highly flexible nature of the porphine skeleton, not limited to deformations taken normal to the mean plane, is an outgrowth of our study of nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester. This biologically interesting porphyrin crystallizes in a rather complex triclinic pattern which is laborious to determine and to describe, but is free of intrinsic packing disorder. Thus, the stereochemical roles of the acetyl and the methyl propionate groups as substituents on the porphine skeleton are displayed. Comparison of the inner ring systems for porphyrins and phthalocyanines reveals some notable similarities along with some even more remarkable differences.

Experimental

The nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester employed in the present study was prepared by Caughey, *et al.*¹⁴ Crystals grown by the

(13) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).

(14) (a) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, *ibid.*, **84**, 1735 (1962); (b) B. D. McLees, W. Y. Fujimoto, and W. S. Caughey, in preparation.

slow evaporation of a solution of the porphyrin in a mixture of *n*-hexane and benzene were subjected to careful preliminary study by means of oscillation, Weissenberg, and precession photographic techniques and were thereby shown to be triclinic with $a = 15.615 \pm 0.02$, $b = 8.74 \pm 0.01$, $c = 13.57 \pm 0.02$ Å., $\alpha = 101.8 \pm 0.2^\circ$, $\beta = 112.4 \pm 0.2^\circ$, and $\gamma = 86.4 \pm 0.2^\circ$. Choice of the centrosymmetric space group $P\bar{1}$ was supported by a negative test for piezoelectricity and by the subsequent analysis leading to a complete determination of structure. A unit cell containing just two molecules of the porphyrin gave a calculated density of 1.345 g./cc., about 5% less than the measured value of 1.415 g./cc. The presence of a molecule of benzene, which would raise the calculated density to 1.424 g./cc. while accounting on the average for about 5.4% of the total scattering of X-rays by the unit cell became evident during the early stages of structure analysis.

The largest available crystal specimen, a prism of dimensions $0.14 \times 0.18 \times 0.22$ mm., was used in taking three-dimensional intensity data with Mo $K\alpha$ radiation and a scintillation counter on a General Electric spectrometer assembly. The stationary crystal-stationary counter technique was employed, with the background evaluated for each reflection as the mean of the counts taken at $2\theta \pm 1.2^\circ$. Observable reflections were largely confined to the range $(\sin \theta)/\lambda < 0.54$; 3122 independent reflections $\{hkl\}$, representing 71% of the theoretical total for the range explored, were definitely recorded as above background. With a linear absorption coefficient of but 6.4 cm.^{-1} for Mo $K\alpha$ radiation, no correction for variation of absorption with specimen shape or scattering angle was deemed necessary. Evidence for some not otherwise apparent deterioration of the crystal during the extended course of the measurements was provided by observing that the periodically recorded intensities of selected standard reflections decreased slowly with time. The intensity-time relations for the standard reflections were used for approximate correction of the intensity data as a whole to the time at which systematic counter measurements were begun. The probable nature of the changes undergone by the crystal specimen and its bearing on the accuracy of the structure determination are matters for later comment. Reduction of the intensity data by standard procedures to give a set of relative $|F_{hkl}|^2$ values set the stage for the determination of structure as described below.

Determination of Structure. The coordinates of the two nickel atoms lying in twofold general positions,¹⁵ $\pm(x, y, z)$, of $P\bar{1}$ were obtained by inspection of the three-dimensional Patterson synthesis of the $|F|^2$ values. Using the calculated contributions¹⁶ of nickel to determine phases, the first partial Fourier synthesis¹⁷ gave positions for atoms defining the porphine skeleton; all remaining atoms (excepting hydrogen) then appeared in the next cycle of Fourier synthesis. Refinement by

(15) "International Tables for X-Ray Crystallography. Vol. I. Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p. 75.

(16) Atomic form factors were taken from "International Tables for X-Ray Crystallography. Vol. III. Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, pp. 202–205.

(17) Cf. H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Belland Sons, London, 1953, Chapter 7.

Table I. Parameter Data for the Crystalline Structure^a

Atom type	(Coordinate \pm std. dev.) $\times 10^4$			$B, \text{\AA}^2$
	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	
Ni	861 \pm 0	3689 \pm 0	823 \pm 0	2.72
C ₁	78 \pm 4	2396 \pm 7	-2596 \pm 4	3.7
C ₂	-604 \pm 4	1603 \pm 7	-2497 \pm 4	2.8
C ₃	-1342 \pm 4	932 \pm 7	650 \pm 4	3.1
C ₄	-961 \pm 3	1451 \pm 6	1746 \pm 4	2.9
C ₅	1722 \pm 4	4956 \pm 7	4241 \pm 4	3.5
C ₆	2334 \pm 4	5793 \pm 6	4104 \pm 4	3.0
C ₇	3114 \pm 4	6348 \pm 7	968 \pm 4	3.5
C ₈	2789 \pm 4	5746 \pm 7	-102 \pm 4	3.7
C ₉	-954 \pm 4	1305 \pm 7	-875 \pm 4	3.0
C ₁₀	399 \pm 4	3187 \pm 7	2995 \pm 4	3.7
C ₁₁	2674 \pm 4	6105 \pm 7	2544 \pm 5	3.3
C ₁₂	1397 \pm 4	4066 \pm 7	-1328 \pm 4	3.3
C ₁₃	631 \pm 3	3207 \pm 6	-1526 \pm 4	3.1
C ₁₄	-453 \pm 4	1923 \pm 7	-1353 \pm 4	3.1
C ₁₅	-786 \pm 3	1608 \pm 6	208 \pm 4	2.5
C ₁₆	-186 \pm 3	2443 \pm 7	1944 \pm 4	2.8
C ₁₇	1139 \pm 4	4141 \pm 7	3166 \pm 4	3.2
C ₁₈	2157 \pm 3	5486 \pm 6	2959 \pm 4	2.8
C ₁₉	2537 \pm 3	5797 \pm 6	1441 \pm 5	3.0
C ₂₀	1946 \pm 4	4830 \pm 7	-327 \pm 4	3.3
C ₂₁	252 \pm 4	2508 \pm 9	-3596 \pm 4	4.7
C ₂₂	-1384 \pm 4	592 \pm 7	-3347 \pm 5	3.8
C ₂₃	-1310 \pm 5	-21 \pm 9	-4437 \pm 4	4.8
C ₂₄	-2165 \pm 4	-113 \pm 8	-62 \pm 5	4.4
C ₂₅	-1285 \pm 4	1140 \pm 7	2572 \pm 4	3.1
C ₂₆	-2153 \pm 4	166 \pm 9	2259 \pm 5	5.9
C ₂₇	1615 \pm 4	4802 \pm 9	5301 \pm 5	4.7
C ₂₈	3074 \pm 4	6948 \pm 7	4969 \pm 4	3.9
C ₂₉	4030 \pm 4	6189 \pm 8	5340 \pm 6	4.7
C ₃₀	4746 \pm 5	7333 \pm 8	6158 \pm 6	5.0
C ₃₁	6371 \pm 5	7705 \pm 10	7338 \pm 8	6.8
C ₃₂	3979 \pm 4	7380 \pm 8	1668 \pm 5	4.4
C ₃₃	4784 \pm 5	6213 \pm 9	2086 \pm 6	5.2
C ₃₄	5653 \pm 5	7105 \pm 9	2972 \pm 6	5.9
C ₃₅	6254 \pm 6	8551 \pm 12	4777 \pm 8	6.8
C ₃₆	3132 \pm 4	5947 \pm 8	-983 \pm 5	4.8
N ₁	328 \pm 3	2896 \pm 5	-766 \pm 3	2.7
N ₂	-66 \pm 3	2516 \pm 5	1016 \pm 3	2.6
N ₃	1417 \pm 3	4454 \pm 5	2391 \pm 3	3.0
N ₄	1826 \pm 3	4803 \pm 5	640 \pm 3	3.2
O ₁	-2048 \pm 3	231 \pm 6	-3187 \pm 3	5.0
O ₂	-874 \pm 3	1669 \pm 6	3540 \pm 3	5.3
O ₃	4639 \pm 5	8691 \pm 8	6435 \pm 8	11
O ₄	5573 \pm 3	6733 \pm 6	6528 \pm 5	5.7
O ₅	6360 \pm 3	7217 \pm 8	2878 \pm 5	8.9
O ₆	5484 \pm 4	7692 \pm 7	3859 \pm 5	7.1
C ₃₇	4593 \pm 6	30 \pm 14	8952 \pm 10	11
C ₃₈	5058 \pm 8	-1321 \pm 17	9153 \pm 10	13
C ₃₉	4485 \pm 6	1295 \pm 14	9666 \pm 9	12

^a Complete amplitude data have been submitted as Document No. 8299 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting in advance \$2.50 for photoprints or \$1.75 for 35-mm. film by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

least-squares procedures with use in the later stages of anisotropic thermal parameters for individual atoms led to the final structural parameters and a conventional R value of 0.099 for the 3122 independent $\{hkl\}$ reflections. The function minimized by the refinement program¹⁸ was $\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$, with $w^{1/2} = 1$ for $|F_o| < 39$, and $w^{1/2} = 39/|F_o|$ for $|F_o| > 39$; approximately 90% of the terms was thereby included at full weight. With 50 atoms (exclusive of hydrogen) in the asymmetric unit of structure and with three positional and six anisotropic thermal parameters for each atom, the total number of variable parameters, including scale factor, was 451; the ratio of the number of independent $\{hkl\}$ intensities to the number of

parameters was then just 3122/451 or 6.9. Qualitative validity, but no very detailed quantitative significance, could then be ascribed to the pattern of anisotropic thermal parameters.

Coordinates with estimated standard deviations for all atoms are given in Table I. Also listed are individual thermal parameters from the final cycle of isotropic least-squares refinement. Forty-seven of these atoms (see Figure 1) comprise the heavy-atom skeleton of the porphyrin molecule. Pseudo-isotropic thermal parameters for the 25 atoms, including nickel, of the porphine skeleton lie in the range from 2.5 to 3.7 \AA^2 ; larger values, generally increasing with the distance from the central nickel atom, characterize atoms in the substituent side chains. It appears, however, that the thermal motions of all atoms in the molecule are quite

(18) Written for the CDC 1604 computer by R. A. Jacobson, *et al.*, at Princeton University, Princeton, N. J.

anisotropic—that, indeed, the ratio of the largest to the smallest values of the thermal parameter lies between 2 and 3 for the typical atom in the porphine skeleton and tends to be still larger for atoms in side chains.¹⁹ Both the Fourier synthesis of electron density and the extraordinarily large thermal parameters (Table I) of the benzene carbon atoms suggest incomplete occupancy of the positions assigned to benzene molecules. It is probable that slow loss of a part of the benzene of crystallization was responsible for the observed slow decrease in periodically recorded intensities of the standard reflections (*vide supra*). The total loss of scattering power from the unit cell could scarcely have exceeded 3%, but, of course, the general level of coherently scattered intensities was rather more strongly affected. Radiation-induced chemical disintegration, a possible alternative source of difficulty, has not appeared to be significant during the taking of data from two other crystalline porphyrins.

Discussion of Results

Molecular bond lengths and angles are listed in Table II; specific bond parameters of the porphyrin molecule are readily identified by consulting Figure 1. Standard deviations of 0.007–0.008 Å. for Ni–N bonds, about 0.010 Å. on the average for C–N and C–C bonds in the porphine skeleton, and rising to 0.015 Å. or more for bonds in the side chains at relatively large distances from the nickel atom are formally computed by the least-squares program. The corresponding range in angular standard deviations is from 0.35° for bond angles at nickel to about 1.0° for angles at the ends of the side chains. Based upon earlier experience^{6,20} in the application of this program to rather better experimental data than those of the present study, we suggest that standard deviations running about 50% larger than those cited above are more realistic. When dealing with individual bond distances, excepting only those of the Ni–N type, a rounding-off to the nearest 0.01 Å. (as in Table II) is appropriate. A set of suitably averaged bond parameters shortly to be described affords maximum simplicity and utility.

Figure 2, which indicates wherein the porphyrin molecule departs from a planar configuration, is obtained directly from Figure 1 through replacement of the symbol designating each atom by the experimentally derived distance of the atom from the mean plane of the porphine skeleton. We see that the porphine skeleton, including the eight carbon atoms directly attached to it, is somewhat ruffled. Closer examination of the structural data discloses, however, that the porphine skeleton is everywhere characterized by a local flatness in the following sense: the three bonds connecting any nitrogen or carbon atom to its three immediate neighbors, or, alternatively, the four-atom groupings thus defined are in every case virtually coplanar. Similarly flat bond systems radiate from the acetyl (C₂₂ and C₂₅) and the carboxylate (C₃₀ and C₃₄) carbon atoms; further, the pyrrole rings are

(19) We have also recast the 300 apparent thermal parameters to give *B* values corresponding to the principal axes of the 50 thermal ellipsoids and the orientations of these latter with respect to the crystal axes; the asymmetric packing relations in the crystal effectively preclude any simple interpretation.

(20) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, 3, 34 (1964).

Table II. Molecular Bond Data

Bond	Length, Å.	Bond	Length, Å.	Bond	Length, Å.
C ₁ –C ₂	1.37	C ₈ –C ₃₆	1.53	N ₂ –Ni	1.95
C ₁ –C ₁₃	1.43	C ₉ –C ₁₄	1.38	N ₄ –Ni	1.96
C ₁ –C ₂₁	1.50	C ₉ –C ₁₅	1.36	C ₂₂ –O ₁	1.21
C ₂ –C ₁₄	1.45	C ₁₀ –C ₁₆	1.41	C ₂₂ –C ₂₃	1.51
C ₂ –C ₂₂	1.50	C ₁₀ –C ₁₇	1.39	C ₂₅ –O ₂	1.22
C ₃ –C ₄	1.36	C ₁₁ –C ₁₈	1.34	C ₂₅ –C ₂₆	1.52
C ₃ –C ₁₅	1.44	C ₁₁ –C ₁₉	1.40	C ₂₈ –C ₂₉	1.54
C ₃ –C ₂₄	1.50	C ₁₂ –C ₁₂	1.36	C ₂₉ –C ₃₀	1.49
C ₄ –C ₁₆	1.44	C ₁₂ –C ₂₀	1.36	C ₃₀ –O ₄	1.19
C ₄ –C ₂₅	1.47	C ₁₂ –Ni	1.37	C ₃₀ –O ₂	1.31
C ₅ –C ₆	1.33	C ₁₄ –N ₁	1.40	O ₄ –C ₃₁	1.48
C ₅ –C ₁₇	1.45	C ₁₅ –N ₂	1.38	C ₃₂ –C ₃₂	1.57
C ₅ –C ₂₇	1.54	C ₁₆ –N ₂	1.36	C ₃₃ –C ₃₄	1.55
C ₆ –C ₁₈	1.44	C ₁₇ –N ₃	1.36	C ₃₄ –O ₅	1.17
C ₆ –C ₂₈	1.54	C ₁₈ –N ₃	1.38	C ₃₄ –O ₆	1.32
C ₇ –C ₈	1.34	C ₁₉ –N ₄	1.41	O ₆ –C ₃₅	1.46
C ₇ –C ₁₉	1.44	C ₂₀ –N ₄	1.40	C ₃₇ –C ₃₈	1.37 ^a
C ₇ –C ₃₂	1.54	N ₁ –Ni	1.98	C ₃₇ –C ₃₉	1.48 ^a
C ₈ –C ₂₀	1.48	N ₂ –Ni	1.95	C ₃₈ –C ₃₉	1.36 ^a

Angle	Deg.	Angle	Deg.	Angle	Deg.
C ₂ C ₁ C ₁₃	106.8	C ₁ C ₁₃ C ₁₂	122.1	C ₉ C ₂₂ O ₁	122.9
C ₂ C ₁ C ₂₁	129.8	C ₁ C ₁₃ N ₁	111.4	C ₉ C ₂₂ C ₂₃	117.5
C ₁₃ C ₁ C ₂₁	123.3	C ₁₃ C ₁₃ N ₁	126.4	O ₁ C ₂₂ C ₂₃	119.6
C ₁ C ₂ C ₁₄	106.6	C ₂ C ₁₄ C ₉	126.5	C ₁ C ₂₅ O ₂	121.6
C ₁ C ₂ C ₂₂	130.2	C ₂ C ₁₄ N ₁	109.8	C ₁ C ₂₅ C ₂₆	121.3
C ₁₄ C ₂ C ₂₂	123.2	C ₉ C ₁₄ N ₁	123.6	O ₂ C ₂₅ C ₂₆	117.0
C ₄ C ₃ C ₁₅	106.1	C ₃ C ₁₅ C ₉	122.2	C ₆ C ₂₈ C ₂₉	111.3
C ₄ C ₃ C ₂₄	132.0	C ₃ C ₁₅ N ₂	111.6	C ₂₈ C ₂₉ C ₃₀	110.8
C ₁₅ C ₃ C ₂₄	122.0	C ₉ C ₁₅ N ₂	126.1	C ₂₉ C ₃₀ O ₃	126.4
C ₃ C ₄ C ₁₆	106.1	C ₄ C ₁₆ C ₁₀	123.2	C ₂₉ C ₃₀ O ₄	113.4
C ₃ C ₄ C ₂₅	127.9	C ₄ C ₁₆ N ₂	112.3	O ₃ C ₃₀ O ₄	120.1
C ₁₆ C ₄ C ₂₅	125.9	C ₁₀ C ₁₆ N ₂	124.5	C ₃₀ O ₄ C ₃₁	120.8
C ₆ C ₅ C ₁₇	106.5	C ₅ C ₁₇ C ₁₀	122.3	C ₃₀ O ₄ C ₃₃	105.5
C ₆ C ₅ C ₂₇	129.3	C ₅ C ₁₇ N ₃	111.2	C ₃₂ C ₃₃ C ₃₄	110.6
C ₁₇ C ₅ C ₂₇	124.2	C ₁₀ C ₁₇ N ₃	126.5	C ₃₃ C ₃₄ O ₅	125.0
C ₅ C ₆ C ₁₈	107.3	C ₆ C ₁₈ C ₁₁	122.9	C ₃₃ C ₃₄ O ₆	109.9
C ₅ C ₆ C ₂₈	128.0	C ₆ C ₁₈ N ₃	110.6	O ₅ C ₃₄ O ₆	125.1
C ₁₈ C ₆ C ₂₈	124.7	C ₁₁ C ₁₈ N ₃	126.6	C ₃₄ O ₆ C ₃₅	116.0
C ₈ C ₇ C ₁₉	108.9	C ₇ C ₁₉ C ₁₁	126.2	N ₁ NiN ₂	90.8
C ₈ C ₇ C ₃₂	129.4	C ₇ C ₁₉ N ₄	110.5	N ₁ NiN ₃	178.5
C ₁₉ C ₇ C ₃₂	121.6	C ₁₁ C ₁₉ N ₄	123.2	N ₁ NiN ₄	89.3
C ₇ C ₈ C ₂₀	105.8	C ₈ C ₂₀ C ₁₂	124.3	N ₂ NiN ₃	90.1
C ₇ C ₈ C ₃₆	130.8	C ₈ C ₂₀ N ₄	110.6	N ₂ NiN ₄	177.8
C ₂₀ C ₈ C ₃₆	123.4	C ₁₂ C ₂₀ N ₄	125.1	N ₃ NiN ₄	89.8
C ₁₄ C ₉ C ₁₅	125.2	C ₁₃ N ₁ C ₁₄	105.3	C ₃₈ C ₃₇ C ₃₉	111.5 ^a
C ₁₆ C ₁₀ C ₁₇	122.1	C ₁₅ N ₂ C ₁₆	104.0	C ₃₇ C ₃₈ C ₃₉	129.3 ^a
C ₁₈ C ₁₁ C ₁₉	124.3	C ₁₇ N ₃ C ₁₈	104.4	C ₃₈ C ₃₉ C ₃₇	119.1 ^a
C ₁₃ C ₁₂ C ₂₀	123.9	C ₁₉ N ₄ C ₂₀	104.0		

^a In benzene molecule.

essentially planar. We note, however, that the plane defined by the bonds radiating from the acetyl carbon atom C₂₂ is rotated about 17° from coincidence with the plane of the pyrrole ring on which the acetyl is substituent. The analogous failure of exact coincidence in the case of the other acetyl substituent is only 2–3°.

The averaged bond parameters displayed in Figure 3 comprise the most useful set consonant with objective criteria of accuracy that is obtainable from the present study. Bond parameters within the porphine skeleton are averaged in agreement with 4mm (C_{4v}) or, effectively, 4/mmm (D_{4h}). Deviations from these averaged values, which the presence of asymmetrically substituted side chains and the stresses attending the asymmetric packing of the molecules would be expected to produce, cannot be objectively confirmed by the present data.²¹

(21) This porphyrin seems especially promising for low temperature

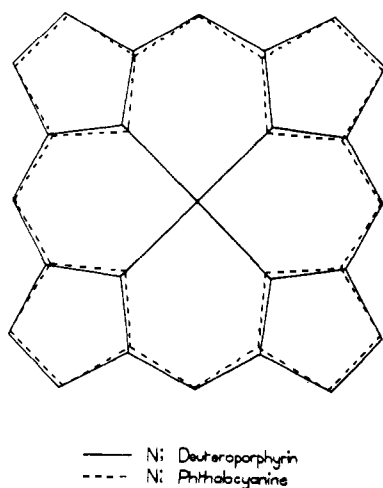


Figure 4. Superposition diagram of the inner skeletons of the NiDeut and nickel phthalocyanine molecules.

corresponding radius in the phthalocyanines, to nitrogen atoms N_m instead of methine carbons, comes out as 3.38 Å. for both phthalocyanine and its nickel derivative.⁷ Taking at face value, for the moment, the bond parameters from the two-dimensional X-ray structure analyses of the phthalocyanines, the superposition

Table IV. Averaged Bond Data for the Central Skeleton in Porphyrins and Phthalocyanines

	Distances, Å.					
	M-N	N-C _q	C _q -C _p	C _p -C _p	C _m -C _q	Ct.-C _m
NiDeut	1.960	1.383	1.446	1.350	1.375	3.402
CuTPP	1.981	1.385	1.449	1.337	1.369	3.403
PdTPP	2.009	1.373	1.436	1.346	1.400	3.412
ClHem	2.062	1.384	1.449	1.337	1.378	3.412
OFeMes	2.073	1.395	1.466	1.368	1.377	3.435
NiEtio	1.957	1.396	1.427	1.335	1.398	<i>a</i>
TPP _{Te}	2.054 ^b	1.350	1.438	1.362	1.403	3.413
TPP _{Tr}	2.065 ^b	1.370	1.442	1.351	1.400	<i>c</i>
PHC	1.92 ^b	1.34	1.49	1.39	1.34 ^d	3.38 ^d
NiPHC	1.83	1.39	1.46	1.38	1.39 ^d	3.38 ^d

	Bond angles, deg.					
	C _q -NC _q	NC _q C _p	C _q C _p -C _p	NC _q -C _m	C _q C _m -C _q	Ct.-NC _q
NiDeut	104.4	110.0	106.8	125.3	123.9	127.8
CuTPP	107.8	107.9	108.1	127.3	123.1	125.9
PdTPP	106.4	109.5	107.3	124.9	125.0	126.8
ClHem	106.1	109.4	107.6	124.9	125.9	126.7
OFeMes	107.0	109.1	107.4	125.9	124.1	126.4
NiEtio	104.9	109.6	107.9	126.7	<i>a</i>	127.8
TPP _{Te}	108.9	108.7	106.9	126.1	125.2	125.5
TPP _{Tr}	107.7	108.8	107.4	126.2	125.6	<i>c</i>
PHC	108.5	110.5	105.3	131	117 ^d	126 ^d
NiPHC	99	115.5	105	126	117 ^d	130.5 ^d

^a Coordinates for methine carbon apparently not reported¹⁰ correctly. ^b Ct.-N distance (Ct. ≡ center of skeleton). ^c Required coordinates not reported in communication.¹¹ ^d N_m replaces C_m .

diagram (Figure 4) of the inner skeletons of NiDeut and NiPHC is obtained; the corresponding diagram for the metal-free porphyrin and phthalocyanine molecules is very much like that of Figure 4. We then ask in what respects the inner skeletons of porphyrin and phthalocyanine molecules differ significantly.

In the tetraphenylporphine molecule of S_4 symmetry^{5,6} the radius of the central hole is $Ct.-N = 2.054 \pm 0.005$ Å.²⁴; the Ni-N (or Ct.-N) distance in the two nickel porphyrins (Table IV) is smaller by 0.095 ± 0.009 Å. The analogous radii for phthalocyanine and its nickel derivative, 1.92 and 1.83 Å., must carry rather large standard deviations, estimated as 0.02 and 0.03 Å. for PHC and NiPHC, respectively. A recent three-dimensional X-ray analysis of structure for crystalline copper phthalocyanine by C. J. Brown (privately communicated) gives a Cu-N bond distance of 1.935 Å., some 0.046 Å. less than that recorded for copper tetraphenylporphine.⁹ This result suggests that the Ni-N bond length in nickel phthalocyanine might be in the neighborhood of 1.90 Å., *i.e.*, longer by two to three standard deviations than the 1.83 Å. earlier reported.⁷ Our over-all assessment is that the Ct.-N radii of the metal-free porphyrin and phthalocyanine molecules probably differ by ≥ 0.10 Å. and that a substantial part of this difference—perhaps half—is maintained in the corresponding metal derivatives.

Reference to Figure 4 suggests that the larger part of the difference in M-N bond distances or Ct.-N radii as between corresponding porphyrin and phthalocyanine species is traceable to a substantial difference between bond angles at the methine carbon (C_m) and its nitrogen replacement (N_m). Reference to Table IV shows indeed that $C_qC_mC_q$ bond angles lie in the range $123.1-125.9^\circ$ and average 124.8° for the more accurately determined structures, whereas $C_qN_mC_q$ angles of 117° are reported for both phthalocyanines. Some part of this 8° difference in angles might disappear in a more accurate evaluation of the phthalocyanine bond parameters. We note, however, that the angle at nitrogen in heteroaromatic systems generally is found to be less than 120° , presumably in consequence of electron repulsions involving the lone pair on the trigonally hybridized nitrogen atom. It is plausible also that the redistribution of charge attending replacement of N_m by HC_m should give a $C_qC_mC_q$ angle greater than 120° .

Table V lists bond orders for the porphine skeleton in the NiDeut molecule as evaluated by two of the several approaches which have used experimentally determined bond lengths to this end. The MO bond orders in the third column were read from bond order vs. bond length curves constructed by Lofthus²⁵ with the aid of molecular orbital theory; orders of 1 and 2 correspond to the respective bond lengths 1.543 and 1.335 Å. for C-C links and to 1.474 and 1.274 Å. for C-N links. The π -bond orders in the fourth column were computed following Cruickshank and Sparks²⁶; π -bond orders of 0 and 1 for C-C links correspond, respectively, to a pure σ -bond of length 1.48 Å. between two trigonally hybridized carbon atoms and a

(24) NOTE ADDED IN PROOF. From the accurate structure determination for crystalline porphine reported in brief by L. E. Webb and E. B. Fleischer, *J. Am. Chem. Soc.*, **87**, 667 (1965), we obtain $Ct.-N = 2.051 \pm 0.003$ Å. In this and in the tetraphenylporphine⁶ studies, the positions of the four "half-hydrogen" atoms attached to nitrogen are clearly delineated on the Fourier difference maps. See also E. D. Becker, R. B. Bradley, and J. C. Watson, *ibid.*, **83**, 3743 (1961).

(25) A. Lofthus, *Mol. Phys.*, **2**, 367 (1959); *cf.* T. H. Goodwin and A. L. Porte, *J. Chem. Soc.*, 3595 (1956).

(26) D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. (London)*, **A258**, 270 (1960); D. W. J. Cruickshank, *Tetrahedron*, **17**, 155 (1962).

Table V. Bond Orders in the Porphine Skeleton

Bond type	Length, Å.	MO bond order	π -Bond order	Kekulé approxn.
N-C _q	1.383	1.39	0.2 ^a	1/4
C _q -C _p	1.446	1.40	0.18	1/4
C _p -C _p	1.350	1.92	0.88	8/4
C _m -C _q	1.375	1.81	0.67	1/2

^a This estimate corresponds to 1.42 Å. for the length of a trigonally hybridized C-N σ -bond and 1.274 Å. for a C=N double bond. See text.

Table VI. Intermolecular Contact Distances, Å.^a

Bond	Length, Å.	Bond	Length, Å.
$x, y + 1, z$		C ₂ -N ₃	3.59
O ₃ -C ₂₈	3.40	C ₅ -O ₃	3.61
O ₃ -C ₃₇	3.49	C ₁₃ -N ₃	3.62
C ₃₁ -C ₃₇	3.71	C ₁₇ -C ₂₁	3.62
$x, y, z + 1$		C ₁₅ -N ₄	3.64
O ₂ -C ₂₁	3.54	C ₂₂ -C ₂₈	3.64
O ₂ -C ₂₃	3.66	C ₁₁ -C ₂₂	3.64
$x + 1, y + 1, z + 1$		C ₁₄ -N ₄	3.66
C ₃₅ -O ₁	3.17	O ₁ -C ₂₈	3.67
C ₂₁ -C ₂₄	3.60	C ₁₈ -Ni	3.68
C ₂₅ -C ₂₃	3.76	C ₂ -C ₁₁	3.68
C ₃₁ -O ₁	3.76	C ₁₄ -C ₁₉	3.68
$\bar{x}, \bar{y}, \bar{z}$		C ₁₈ -O ₁	3.69
C ₂₃ -O ₂	3.48	C ₂₃ -C ₂₈	3.70
C ₁ -C ₂₅	3.52	C ₁₁ -C ₁₄	3.70
C ₂ -C ₄	3.54	C ₁₄ -C ₁₈	3.71
C ₉ -C ₁₅	3.59	C ₁₄ -N ₃	3.73
C ₁₀ -C ₂₂	3.60	C ₂ -C ₆	3.74
C ₉ -N ₂	3.61	C ₈ -C ₁₅	3.75
C ₃ -C ₁₄	3.61	C ₁ -C ₁₈	3.76
C ₃ -N ₁	3.62	C ₉ -C ₁₁	3.76
C ₁₀ -C ₂₃	3.62	C ₇ -C ₂₄	3.77
N ₁ -C ₂₄	3.63	Ni-Ni	3.77
C ₄ -C ₁₄	3.65	C ₁₅ -N ₂	3.77
C ₂ -C ₂₅	3.70	C ₁₅ -C ₁₉	3.78
C ₁₅ -C ₁₅	3.71	Ni-N ₃	3.79
O ₂ -C ₂₁	3.73	$\bar{x}, \bar{y}, \bar{z} + 1$	
C ₁ -C ₂₅	3.75	C ₂₆ -C ₃₈	3.53
C ₂₅ -C ₂₁	3.76	C ₂₆ -C ₃₉	3.70
C ₂₆ -C ₂₁	3.78	$\bar{x} + 1, \bar{y} + 1, \bar{z}$	
C ₁ -C ₄	3.78	O ₅ -C ₃₆	3.64
C ₁₆ -C ₂₂	3.79	$\bar{x}, \bar{y} + 1, \bar{z} + 1$	
C ₂ -C ₁₆	3.80	O ₂ -C ₂₇	3.50
C ₁₀ -O ₁	3.80	$\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$	
C ₂₄ -Ni	3.80	C ₂₉ -O ₄	3.42
$\bar{x}, \bar{y} + 1, \bar{z}$		C ₁₈ -C ₃₁	3.56
C ₁₁ -O ₁	3.33	C ₁₁ -C ₃₁	3.57
C ₂ -C ₁₈	3.39	C ₁₁ -O ₄	3.61
N ₁ -Ni	3.41	O ₅ -C ₃₈	3.65
C ₉ -C ₁₉	3.42	O ₄ -C ₃₈	3.66
C ₁₅ -C ₂₀	3.51	O ₅ -C ₃₉	3.67
C ₁ -N ₂	3.53	C ₃₂ -C ₃₈	3.69
C ₁ -C ₁₇	3.53	C ₂₉ -O ₆	3.72
C ₁₂ -C ₁₆	3.56	N ₃ -C ₃₁	3.76
C ₁₈ -C ₂₂	3.57	C ₁₉ -C ₃₁	3.78
C ₆ -C ₂₂	3.58	C ₂₇ -O ₅	3.79
C ₁₂ -N ₂	3.58	$\bar{x} + 1, \bar{y} + 2, \bar{z} + 1$	
C ₂₀ -N ₂	3.58	O ₃ -C ₃₅	3.15
C ₉ -N ₄	3.58	O ₃ -O ₅	3.25
C ₃ -C ₈	3.59	O ₃ -C ₃₄	3.64

^a Distances are listed from the standard molecule (x, y, z) to related molecules denoted by their equivalent position.

standard double bond of length 1.335 Å. The partial double bond characters in the fifth column are ob-

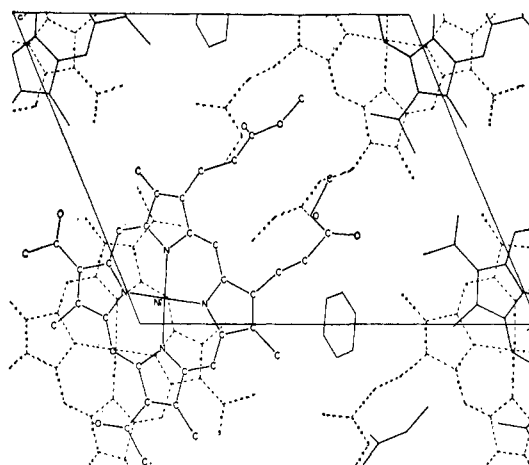


Figure 5. Packing diagram for crystalline NiDeut. The contents of the unit cell are projected onto a plane normal to the b -axis.

tained by simple enumeration of the classical formulas of the Kekulé type.²⁷

The data of Table V suggest substantially less delocalization of π -bonding in the porphine skeleton than any of the published approximate theoretical treatments²⁸⁻³⁰ of the problem would lead one to expect. That adjacent C_p-C_p and C_p-C_q bonds in either a metal-free porphyrin or its metal derivative are of markedly different bond orders is particularly well substantiated experimentally.^{6,9,11} According to the analysis presented earlier,^{5,6} some ruffling or other appropriate departure from planarity of the porphine skeleton should materially reduce angular strain in the pattern of trigonally hybridized σ -bonding. Considering σ -bonding alone, that is, there should be a small energy barrier to reflection of configuration through the mean plane. Although this barrier would be obliterated by an adequately delocalized and sufficiently strong contribution from π -bonding, it is not certain that this is the case of the porphine skeleton. In either event, however, the conclusion^{5,6} that the skeleton should ordinarily behave as if the configurational potential energy had a single broad minimum with respect to deviations from planarity is a good working principle which implies the observed conformational adaptability of the skeleton to the circumstances of its environment.

A ruffling of the porphine skeleton from planarity is present in six of the ten porphyrins listed in Table IV. The ruffling in NiDeut (Figure 2) is both relatively small and irregular; *i.e.*, it follows no required symmetry. A modest convexity of skeleton which characterizes the iron(III) porphyrins thus far investigated is discussed in the accompanying paper,¹³ as is the reportedly planar skeleton in the crystalline dihydrate of zinc(II) tetraphenylporphine.⁹ A more general type of skeletal deformation is observed in triclinic tetraphenylporphine.¹¹

Table VI lists all intermolecular packing distances below 3.8 Å. Figure 5 shows the contents of the unit

(27) Cf. L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 236.

(28) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(29) H. Kobayashi, *ibid.*, **30**, 1373 (1959).

(30) M. Gouterman, G. Wagniere, and L. C. Snyder, *J. Mol. Spectry.*, **11**, 108 (1963).

cell as projected onto a plane perpendicular to the *b*-axis. This axis is the stacking direction for somewhat tilted molecules in parallel array; perpendicular separations between the porphine mean planes of contiguous molecules related by inversion centers at, respectively, the origin and 0, 0.5, 0 are 3.52 and 3.45 Å., to be compared with the analogous interplanar distance of 3.38 in both the NiPHC and PHC structures.

Many close contacts occur between successive overlying molecules (Table VI). The closest of these involving atoms of the porphine skeleton are between molecules related by the inversion center at 0, 1/2, 0 and range upward from 3.33 Å. for C··O, 3.39 Å. for C··C, and 3.53 Å. for C··N distances. Apart from the four nitrogen atoms to which it is bonded (at 1.960 Å.) within the molecule, a nickel atom has no

neighbors closer than a nitrogen at 3.41 Å., a carbon at 3.68 Å., and another nickel atom at 3.77 Å.

The shortest packing separation, 3.15 Å., is between the terminal methyl carbon of a propionic ester chain, C₃₅ in Figure 1, and a carbonyl oxygen of O₃ type in a second molecule related to the first by the inversion center at 1/2, 1, 1/2. Another close contact of 3.17 Å. involves C₃₅ of the first molecule and an oxygen atom of the O₁ type in the molecule obtained from the first by the translation, $\vec{a} + \vec{b} + \vec{c}$.

Benzene is present in the crystal as the uncomplexed solvent of crystallization. A benzene molecule (Figure 5) at the inversion center 1/2, 0, 1 lies between successive stacks of porphyrin molecules with its plane turned 80° from the porphine mean plane.

The Crystal Structure and Molecular Stereochemistry of Methoxyiron(III) Mesoporphyrin-IX Dimethyl Ester¹

J. L. Hoard,^{2,3} M. J. Hamor,² T. A. Hamor,² and W. S. Caughey⁴

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York, and the Department of Physiological Chemistry, The Johns Hopkins School of Medicine, Baltimore, Maryland. Received January 21, 1965

Three-dimensional X-ray diffraction data from monoclinic single crystals of methoxyiron(III) mesoporphyrin-IX dimethyl ester were used to determine structure. Disorder in the packing of molecules within the crystal is traceable to incomplete sorting of the stereochemically not very dissimilar D and L isomers onto their respective sublattices. The iron atom lies 0.49 Å. from the mean plane of the modestly domed porphine skeleton and is limited to five-coordination. Fe-N bond distances average 2.073 ± 0.006 Å., and the Fe-OCH₃ link is 1.842 ± 0.004 Å. A good deal of evidence suggests that substantial displacement of the iron atom from the plane of the nitrogen atoms is a normal structural property of high-spin iron porphyrins.

Introduction

The preceding report⁵ on the structure of nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester particularly emphasizes the stereochemical adaptability of the porphine skeleton to the varying circumstances of its environment. A somewhat different aspect of this theme comes out of the structural study reported herein of another biologically significant porphyrin, methoxyiron(III) mesoporphyrin-IX dimethyl ester (henceforth abbreviated as MeOFeMeso). Background

material beyond that presented in the introductory section of the accompanying paper⁵ includes Kendrew's observation⁶ that in the myoglobin structure the iron atom lies more than 0.25 Å. out of the mean plane of the heme group and his comment⁶ that Koenig had observed a similar phenomenon by structure analysis of hemin. Following structure determination for crystalline MeOFeMeso, we obtained on loan a copy of Koenig's thesis⁷ describing his work on chlorohemin, and found that the two studies give consistent stereochemical descriptions of the pyramidal coordination groups surrounding the Fe(III) atoms (*vide infra*). The recently published structures⁸ for aquohydroxyiron(III) tetraphenylporphine and diaquozinc(II) tetraphenylporphine contain, by comparison, some anomalous features which will require subsequent comment.

Experimental

Purple-black opaque crystals of methoxyiron(III) mesoporphyrin-IX dimethyl ester from a preparation by J. O. Alben and W. S. Caughey (unpublished work) were subjected to careful preliminary study by oscillation and Weissenberg X-ray techniques and were thereby shown to be monoclinic. The absence of piezoelectricity in quite sensitive tests and the subsequent analysis of the statistical distribution of diffraction intensities with $\sin \theta$ suggested I2/m as the most probable space group; the noncentric possibilities, however, were not immediately discarded. Cell dimensions of $a = 11.55 \pm 0.02$, $b = 24.15 \pm 0.03$, $c =$

(1) Support of this work by the National Institutes of Health of the Public Health Service, the National Science Foundation, and the Advanced Research Projects Agency is gratefully acknowledged. We also thank the Cornell Computing Center, John W. Rudan, Director.

(2) Department of Chemistry, Cornell University, Ithaca, N. Y.

(3) Author to whom correspondence should be addressed.

(4) Department of Physiological Chemistry, The Johns Hopkins University, Baltimore, Md.

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

(6) J. C. Kendrew, *Science*, **139**, 1259 (1963).

(7) D. F. Koenig, Thesis, The Johns Hopkins University, (1962); *Acta Cryst.*, in press.

(8) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).