

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

The Structure of Nickel Etioporphyrin-I<sup>1</sup>

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RECEIVED JULY 26, 1962

The crystal structure of nickel etioporphyrin-I was determined. Bond lengths and bond angles were calculated. The molecule is non-planar, being distorted by having two of the pyrrole rings bent up and two bent down from the plane formed by the four-corner methene carbon atoms.

The accurate structure determination of porphyrins has received very little attention. Previous X-ray studies on porphyrins have either been carried out with two-dimensional data<sup>2</sup> or have been of low accuracy.<sup>3</sup>

We have initiated a program for the accurate determination of porphyrin and metalloporphyrin structures. We would like to report the X-ray determination of nickel etioporphyrin-I.

## Experimental

Nickel etioporphyrin-I, C<sub>32</sub>H<sub>36</sub>N<sub>4</sub>Ni, was prepared by refluxing pure etioporphyrin-I<sup>4</sup> with nickel acetate in glacial acetic acid. The product was isolated by the usual techniques. Crystals of the nickel etioporphyrin I were grown by slow evaporation from benzene solutions. The crystals were well-formed, deep purple tetragonal dipyramids. The crystal used for data collection measured 0.25 mm. across the pyramid edge.

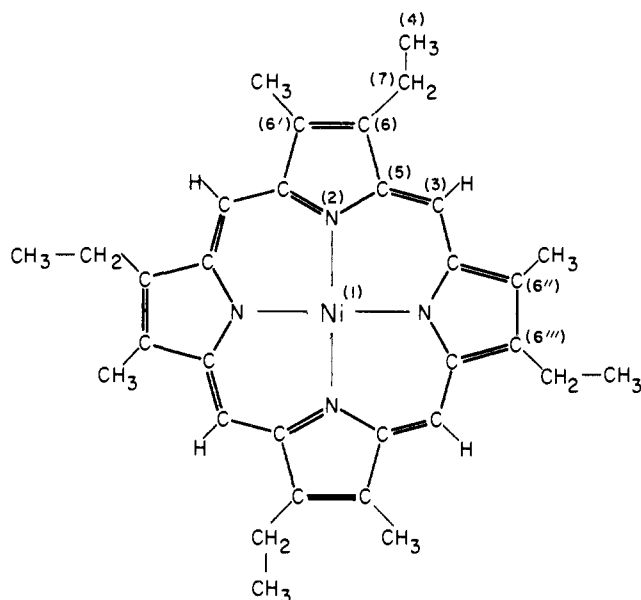


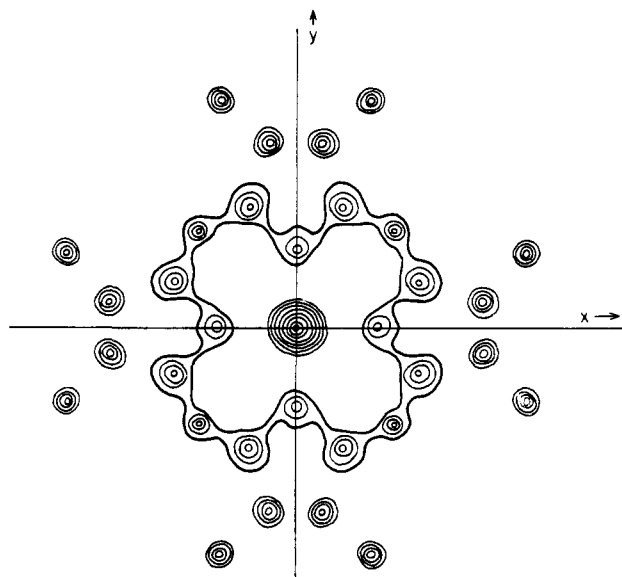
Fig. 1.—Nickel etioporphyrin-I.

The crystal is tetragonal with the cell dimensions:  $a = 14.61 \pm 0.01 \text{ \AA.}$ ,  $c = 12.38 \pm 0.01 \text{ \AA.}$  The unit cell volume is 2643  $\text{\AA.}^3$ . The density of the nickel etioporphyrin-I is 1.35 g./cm.<sup>3</sup>. This gives four molecules per unit cell. Precession photographs were taken to determine the space group. The Laue class is 4/mmm. The following limiting conditions on the reflections were found:

$$\begin{aligned} hkl: h + k + l &= 2n \\ h00: h (k) &= 2n \\ hhl: 2h + l &= 4n \end{aligned}$$

These conditions determine the space group uniquely as  $I4_1/amd$  (no. 141 in the "International Tables of Crystallography"). The data were collected using a scintillation counter with MoK $\alpha$  radiation. (The monochromatic radiation was produced by using a bent quartz crystal monochromator.) The crystal settings were calculated using an IBM 1620 computer.<sup>5</sup>

The intensities of the reflections were determined by integrating the recorder scan of each peak. The integration was carried out with a planimeter. The set of intensities was corrected for Lorentz and polarization factors. The absorption correction was small enough to neglect. The structure factors were placed on an approximate absolute scale by application of Wilson's method.<sup>6</sup>

Fig. 2.—The electron density of nickel etioporphyrin-I at  $z = 0.125$ . Contours are drawn at arbitrary intervals of electron density.

**Determination of the Structure.**—The atoms of the nickel etioporphyrin-I molecule are numbered in Fig. 1. An account of the way the molecules fit into the unit cell can be found in Crute's work on nickel etioporphyrin-II.<sup>3</sup>

The origin of the cell is taken at a center of symmetry at a distance of  $0, -1/4, 1/8$  from the site  $4m2$ . The nickel atoms are at the sites  $4m2$  of multiplicity 4. The molecule, due to the ethyl group, cannot fit into the symmetry of the space group. We have assumed, like Crute, that the molecules are randomly distributed between two enantiomorphous configurations giving a statistical symmetry of  $4m2$ .

The first set of structure factors was calculated<sup>7</sup> using Crute's atomic coordinates.<sup>3</sup> These coordinates were refined using the Least Squares Program.<sup>7</sup> The scattering factors used were those of Watson and Freeman,<sup>8</sup> and of Berghuis.<sup>9</sup>

The final cycle of the least squares calculation of nickel etioporphyrin-I excluding hydrogen atoms and using individual isotropic temperature factors is listed in Tables I and II. Table I gives the observed and calculated structure factors for each measured reflection. Table II gives the final calculated coordinates, temperature factors and standard deviations. The final reliability index,  $R$ , not including zero reflections or the 6 reflections omitted in the final stage of refinement, is 7.4%. The  $R$ -factor including unobserved reflections is 11.7%. Figure 2 shows the electron density of the molecule calculated at the section  $z = 0.125$ .

(6) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(7) The following programs were used for the calculations: W. Busing and H. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704"; W. Busing and H. Levy, "A Crystallographic Function and Error Program for the IBM 704"; D. Van der Helm, "A Fourier Summation Program for the IBM 1620."

(8) R. E. Watson and A. J. Freeman, *Acta Cryst.*, **14**, 27 (1961).(9) J. Berghuis, *et al.*, *ibid.*, **8**, 478 (1955).

(1) This research was supported by a Public Health Service Grant.

(2) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); 1736 (1936); 219 (1937); 36 (1940).(3) M. B. Crute, *Acta Cryst.*, **12**, 24 (1959).

(4) The etioporphyrin I was a gift of E. Markham.

(5) The program for this calculation was written by G. Gibbs.

TABLE IA  
 CALCULATED AND OBSERVED STRUCTURE FACTORS<sup>a</sup>

<i>hkl</i>	$F_{\text{obsd}}$	$F_{\text{calcd}}$	<i>hkl</i>	$F_{\text{obsd}}$	$F_{\text{calcd}}$
200	25.1	25.7 <sup>c</sup>	101 <sup>b</sup>	47.3	-59.7
400 <sup>b</sup>	32.0	-22.4	301	26.0	-24.5
600	27.6	28.7	501	25.4	-24.3
800	18.1	21.8	701	12.0	-14.2
10,0,0	17.2	18.9	11,0,1	19.1	-18.8
14,0,0	13.5	13.7	13,0,1	5.1	-7.6
220 <sup>b</sup>	15.8	22.4	211	7.2	4.7
420	20.9	-21.8	411	28.9	-24.8
620	23.6	-25.2	611	27.7	-28.4
820	27.1	-26.8	811	7.8	-7.5
10,2,0	20.9	-23.2	10,1,1	10.1	-11.5
14,2,0	9.1	-10.4	12,1,1	5.3	-6.5
440	55.3	49.9	14,1,1	11.3	-11.0
640	5.9	6.7	321	15.4	10.3
10,4,0	4.2	3.2	521	13.7	12.9
12,4,0	4.5	4.1	721	25.4	24.8
660	21.6	-21.5	921	9.4	11.2
860	17.9	-18.2	11,2,1	10.2	9.9
10,6,0	3.3	-3.6	431	11.7	10.9
12,6,0	12.9	-15.4	631	5.7	4.6
880	32.3	33.0	831	16.0	17.6
10,8,0	9.3	7.8	10,3,1	9.9	9.9
541	6.7	6.0	422	3.0	-2.0
741	17.5	-17.2	622	5.7	1.4
941	8.7	-8.1	822	3.3	2.1
11,4,1	2.9	2.8	332	21.0	-21.2
13,4,1	2.9	-2.6	532	4.0	-1.0
851	13.0	-12.9	732	29.0	-26.6
10,5,1	6.9	-8.5	932	15.4	-16.6
12,5,1	7.3	-9.0	642	2.3	1.0
761	18.9	18.8	552	10.2	-8.7
961	10.4	10.3	752	21.0	21.7
871	13.6	11.8	952	13.6	12.7
12,7,1	7.3	7.6	11,5,2	4.9	6.0
981	14.7	-13.3	13,5,2	12.4	13.1
11,8,1	3.8	-3.8	772	22.7	-22.8
10,9,1	4.4	-3.8	972	9.9	-10.7
202	11.7	-13.0	992	16.8	16.3
602	4.0	2.4	103	83.0	85.3
112	34.2	36.7	303	7.4	8.3
312 <sup>b</sup>	26.7	20.9	503	6.2	6.8
512	37.1	32.4	703	11.8	13.2
712	29.3	27.4	903	5.0	4.9
912	4.8	4.1	11,0,3	13.6	13.7
11,1,2	21.2	22.1	213 <sup>b</sup>	13.6	7.3
13,1,2	8.5	9.1	413	5.4	-6.3
613	25.6	-24.9	204	18.1	-19.3
813	13.7	-13.4	404	15.5	-16.0
10,1,3	10.9	-12.2	604	27.7	-28.4
323	8.6	-6.0	804	5.2	-6.1
523	15.7	-14.8	10,0,4	13.5	-13.3
723	22.3	-20.9	12,0,4	6.6	-7.9
923	13.8	-14.5	314	4.4	3.2
11,2,3	8.4	-9.1	514	5.2	-4.2
433	23.3	22.5	224	11.0	-10.1
633	4.3	3.8	424	20.5	20.2
833	10.1	11.0	624	22.1	22.5
10,3,3	12.2	11.8	824	21.2	21.6
543	10.6	10.4	10,2,4	17.0	18.6
743	7.9	8.1	534	2.3	1.0
11,4,3	2.8	-1.9	734	5.4	-4.3
13,4,3	6.6	4.3	934	3.0	2.5
653	4.5	-3.3	444	19.5	-18.4
853	6.1	-5.7	644	3.2	-3.4
10,5,3	6.4	-5.6	844	10.3	-10.3
12,5,3	8.7	-10.0	1044	6.0	-5.5
763	16.3	-17.8	754	5.1	5.3
963	7.0	-8.3	11,5,4	3.5	5.4

873	17.1	15.5	664	15.8	15.2
983	16.8	15.7	864	16.8	16.9
10,6,4	5.0	5.1	945	6.9	6.1
974	5.6	-5.2	655	4.4	4.3
884	22.8	-22.6	855	7.9	8.0
105	34.9	34.6	765	15.6	-15.7
305	9.6	10.7	965	7.8	-7.4
505	13.6	13.7	875	10.2	-9.0
705	14.5	14.7	985	13.2	11.9
11,0,7	16.1	17.8	206	23.5	22.6
215	9.3	8.7	606	9.9	-9.4
415	12.4	12.8	116	26.2	-24.5
615	18.0	18.1	316	15.4	-13.2
815	8.9	8.6	516	26.1	-24.3
10,1,5	8.9	9.1	716	20.3	-18.4
12,1,5	7.2	7.4	916	3.6	-3.0
325	12.7	-11.3	11,1,6	14.1	-15.2
525	8.4	-8.0	336	15.0	14.9
725	17.1	-18.0	536	5.3	4.0
925	7.5	-6.5	736	18.9	18.3
11,2,5	9.0	-8.4	936	12.4	14.1
435	9.7	-10.5	646	4.2	4.5
635	6.8	-6.5	556	6.1	6.2
835	12.5	-13.0	756	14.0	-14.5
10,3,5	6.2	-5.5	956	10.8	-10.2
745	16.6	15.5	776	18.7	18.3
			976	8.7	8.4

<sup>a</sup> Multiply  $F_{\text{obsd}}$  by 3.84 to obtain Structure Factors on an absolute scale. <sup>b</sup> Omitted from final stages of refinement. <sup>c</sup>  $F_{\text{calcd}}$  rounded off from machine output.

 TABLE IB  
 CALCULATED STRUCTURE FACTORS OF UNOBSERVED REFLECTIONS

<i>hkl</i>	$F_{\text{calcd}}$	<i>hkl</i>	$F_{\text{calcd}}$
12,0,0	2.5	11,6,3	-4.4
12,2,0	0.0	10,7,3	-1.5
8,4,0	-1.8	7,1,4	0.0
9,0,1	4.3	9,1,4	-2.6
13,2,1	2.2	11,1,4	3.8
12,3,1	-5.9	13,1,4	-2.1
6,5,1	-1.0	12,2,4	0.2
11,6,1	3.9	11,3,4	-0.6
10,7,1	-0.4	12,4,4	0.0
4,0,2	0.3	9,5,4	-0.8
8,0,2	0.7	9,0,5	-0.7
10,0,2	1.8	12,3,5	4.0
12,0,2	-1.7	5,4,5	-0.8
14,0,2	1.2	11,4,5	-0.7
10,2,2	-0.1	10,5,5	5.8
12,2,2	1.5	11,6,5	-0.8
11,3,2	-1.1	10,7,5	0.3
13,3,2	3.0	4,0,6	-0.1
8,4,2	1.3	8,0,6	-2.7
10,4,2	1.3	10,0,6	-0.8
12,4,2	0.0	12,0,6	5.2
8,6,2	-0.8	4,2,6	1.6
10,6,2	0.8	6,2,6	-2.5
12,6,2	0.4	8,2,6	-3.0
11,7,2	-2.3	10,2,6	0.6
10,8,2	-0.9	11,3,6	1.1
12,1,3	-0.4	8,4,6	-2.0
13,2,3	-2.7	8,6,6	-1.6
12,3,3	-3.4	10,6,6	-2.5
9,4,3	0.5		

### Discussion of Results

There are several interesting points that have resulted from this work. One is that this metalloporphyrin is not a planar molecule. That this is a general result for all porphyrins is a conclusion that must await further work on other porphyrins.

The non-planarity can be described in the following manner. The nickel atom (1) and the four corner

TABLE II  
 ATOMIC COÖRDINATES, TEMPERATURE FACTORS AND STANDARD DEVIATIONS

Atom	Code number	$x$	$\sigma_x^a$	$y$	$\sigma_y$	$z$	$\sigma_z$	$B^b$
$1/8$ Ni	1	0.50000		0.25000		0.12500		3.02
$1/2$ N	2	.36610	0.00087	.25000		.11947	0.00154	3.47
$1/2$ C	3	.33126	.00155	.41874	0.00155	.12500		3.68
$1/2$ C	4	.11082	.00197	.37290	.00200	-.02811	0.00457	6.40
C	5	.30791	.00079	.32573	.00077	.11572	.00116	3.43
C	6	.21541	.00080	.29568	.00081	.10499	.00116	3.78
C	7	.13227	.00096	.36124	.00103	.09360	.00221	5.19

<sup>a</sup> Standard deviations as calculated by least squares program. <sup>b</sup>  $B$  is the individual isotropic temperature factor. <sup>c</sup> Fixed by symmetry.

 TABLE III  
 INTRAMOLECULAR BOND LENGTHS

Bond	Length in Å.	Standard deviation
1-2	1.957	0.013
2-5	1.396	.013
3-5	1.398	.013
5-6	1.427	.016
6-6'	1.335	.023
6-7	1.554	.018
7-4	1.542	.039

 TABLE IV  
 BOND ANGLES

Angle <sup>a</sup>	Angle in degrees	Standard deviation
1,2,5	127.6	0.7
2,5,6	109.6	1.0
2,5,3	126.7	1.4
3,5,6	123.6	1.3
6,7,4	108.6	1.6
5,6,7	124.0	1.1

<sup>a</sup> Middle number is vertex of angle.

methene atoms (3) form a plane parallel to the 001 plane at  $z = 0.125$ . We will discuss the deviation of the other atoms in the molecule from this defined plane. The pyrrole nitrogen atom (2) lies slightly out of the plane but only at the limit of significance. (We shall take three times the standard deviation as the limit of significance.) On the other hand, the carbon atoms (5) and (6) are significantly out of the above defined plane. The molecular symmetry is such that two of the pyrrole rings are bent up and two are bent down from the plane. If one defines a plane by the atoms

(6) and (6') and their mirror images, then the perpendicular distance between this plane and the reference plane is 0.25 Å. This is a considerable distortion of the molecule from planarity.

It cannot be determined if the non-planarity of the porphyrin ring is caused by the nickel atom pushing on the pyrrole nitrogens to cause a distortion. The nickel-nitrogen distance does not seem excessively small to cause this type of distortion. In order to solve the problem, a free base porphyrin structure will have to be determined.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

## Electronegativity. II. Bond and Orbital Electronegativities<sup>1,2</sup>

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RECEIVED APRIL 26, 1962

A new definition for electronegativity is proposed as  $\chi = dE(n)/dn$ , where  $E(n)$  is the energy of an atom in its valence state as a function of the occupation,  $n$ , of the orbital for which the electronegativity is expressed. This definition is found for singly occupied orbitals to be identical with Mulliken's definition of electronegativity. The given representation, although equivalent to previous concepts, permits in addition the computation of *orbital electronegativities* of vacant and doubly occupied orbitals and of groups. A new term *bond electronegativity* is defined, as the electronegativity of orbitals forming a bond, after charge has been exchanged between them. It is shown that this process of charge exchange will equalize the electronegativity of the two orbitals forming a bond to lower the energy of the molecule. Such a treatment leads directly to a new definition and clear understanding of ionic character in terms of charge transferred between the bond-forming orbitals.

The concept of electronegativity has had extremely wide use and considerable success in systematizing experimental chemical data. Nonetheless, it has never been quite adequately defined. Thus, in recent numerical work on electronegativities,<sup>1</sup> it was necessary to define the concept of orbital electronegativity to indicate that this is a property, not of the atom as such, but of an individual orbital of the atom. In addition it seemed again unreasonable that this quantity was measured in units of energy (e.g., eV.). Pauling's<sup>3</sup> verbal definition of electronegativity: "The power of an atom in a molecule to attract electrons to itself" suggests, not the units of energy, but of potential, *i.e.*, energy/charge. This was recognized recently by Iczkowski and Margrave,<sup>4</sup> who redefined electro-

negativity as a derivative of energy with respect to charge. Their definition is not completely satisfactory; first, it ignores completely the orbital dependence of electronegativity; second, it assumes that the energy of an atom is a continuous and single-valued function of its charge. That the function is not single-valued is apparent from the fact that a variety of different valence states with different energies are readily obtained for a given element.<sup>1</sup> For trigonally hybridized carbon, when the charge is +1 or -1, we have reported two energies,<sup>1</sup> considerably different, depending on the distribution of the electrons.

We have developed a definition of electronegativity (or better orbital electronegativity) which is mathematically defensible—although based on some assumptions—and which promises to be extremely useful in all the areas in which electronegativity has generally been applied. Since this definition is capable of sen-

(1) Paper 1 of this series, J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(2) This work was supported by a contract with Materials Central, Wright Air Development Division, U. S. Air Force.

(3) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(4) R. P. Iczkowski and J. L. Margrave, *ibid.*, **83**, 3547 (1961).