37. *An X-Ray Study of the Phthalocyanines. Part III. Quantitative Structure Determination of Nickel Phthalocyanine.*

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IN a recent paper (J., 1936, 1195) it was shown that the phase constants of the *X*-ray reflections from crystals of phthalocyanine and its nickel derivative could be determined by comparing absolute measurements of the corresponding structure factors. This led to a direct metrical determination of the structure of the metal-free compound, by the method of Fourier analysis, with results in agreement with the chemical structure assigned by Linstead (J., 1934, 1016). Some small distortions from regularity were found to exist in the molecule, and it was thought these might be caused by internal hydrogen bonds connecting opposite pairs of *iso*indole nitrogen atoms. In order to obtain further information on this point and, in particular, to study the effect on the inner nucleus of the presence of a co-ordinating metal atom, we have now completed an independent Fourier analysis of the nickel phthalocyanine structure. Both structures have been verified by computing all the structure factors from the co-ordinates assigned to the atoms. These results are given in the experimental section (Table V).

The crystal data for nickel phthalocyanine, $C_{32}H_{16}N_8Ni$, are: space group C_{2h}^5 ($P2_1/a$), $a = 19{\cdot}9$, $b = 4{\cdot}71$, $c = 14{\cdot}9$ A., $\beta = 121{\cdot}9°$, with two centrosymmetrical molecules per unit cell of volume 1186 A.^{3}; d(found) = 1·63, (calc.) = 1·59, $M = 571$, $F(000) = 584$. The linear dimensions are almost identical with those of free phthalocyanine.

The method of finding the phase constants has already been described (*loc. cit.*, p. 1197), and in fact the determinations made for free phthalocyanine carry with them corresponding determinations for nickel phthalocyanine. It should be noted, however, that the results described below are derived from an entirely independent set of intensity measurements, made upon crystals of nickel phthalocyanine. The structure factors derived from these measurements, with the phase constants for the ($h0l$) zone, are collected in Table I.

TABLE I.

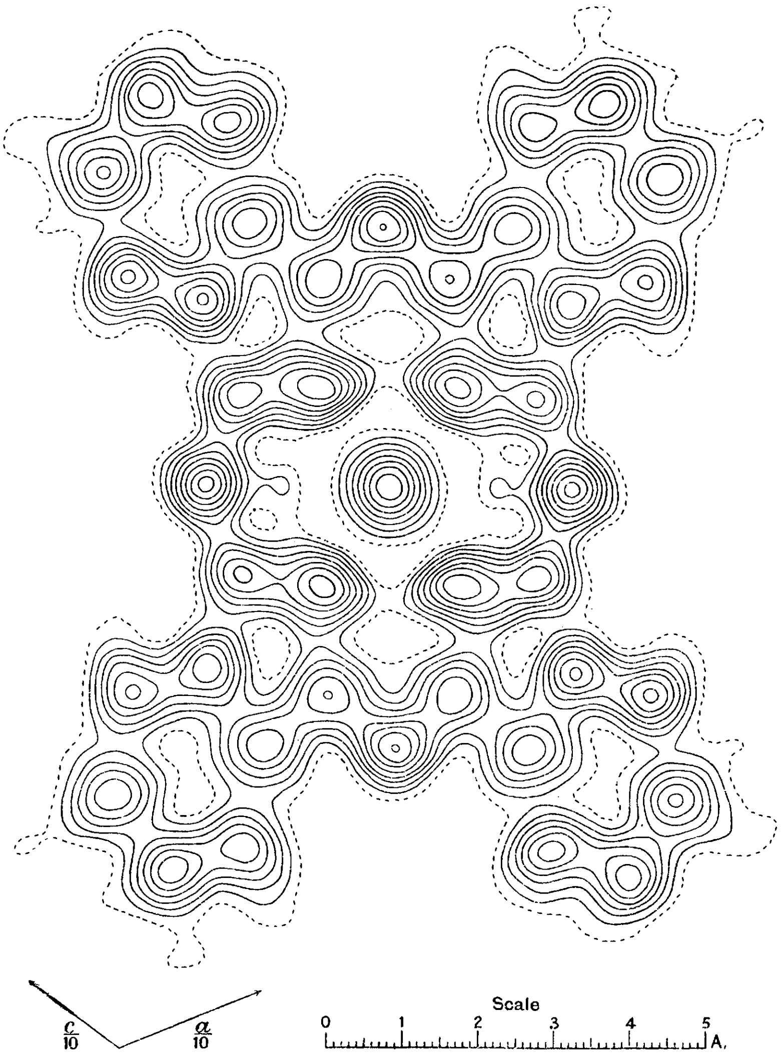
Values and Signs of $F(h0l)$.

l.	*h.*										
	0	2	4	6	8	10	12	14	16	18	20
11	+ 16	—	—	—	—	—	—	—	—	—	—
10	+ 34	− 20	—	—	—	—	—	—	—	—	—
9	+ 17·5	—	+ 27	—	—	—	—	—	—	—	—
8	—	+ 38·5	+ 21·5	+33	—	—	—	—	—	—	—
7	+ 57	+ 51	+ 34·5	+78	+26	—	—	—	—	—	—
6	− 17·5	+ 25·5	+ 57·5	+50	+42	+16	—	—	—	—	—
5	− 12·5	− 29	—	+49·5	—	—	—	—	—	—	—
4	+ 55·5	+ 55·5	− 28	+43	+40·5	—	−15·5	—	—	—	—
3	—	+ 31	+ 46	—	+28·5	+35·5	+21·5	+18	—	—	—
2	− 36·5	+ 54	+ 49·5	−40	+49·5	—	—	+17·5	+24	—	—
1	+112	− 43	+ 28·5	—	+30·5	+26·5	+21·5	−15	—	—	—
0	+584	+ 55	—	+80·5	+44	+43·5	+40·5	+14·5	—	—	—
$\bar{1}$	+112	+136·5	+129	—	+58·5	+94·5	+38	+25	—	—	—
$\bar{2}$	− 36·5	+ 71·5	− 46	−10·5	+30	+50·5	+21·5	+25·5	+28·5	—	—
$\bar{3}$	—	+112·5	− 29·5	+ 9·5	+54·5	+60·5	+15	—	+16·5	+12·5	—
$\bar{4}$	+ 55·5	− 10·5	—	+44·5	+38	+44	+81	+14·5	—	+38	—
$\bar{5}$	− 12·5	+ 73·5	—	+24·5	+22	+17	+29·5	+35	+17	+36	—
$\bar{6}$	− 17·5	+ 37·5	+ 32·5	+65·5	+42	+59	−21·5	+39·5	+30·5	+14·5	+12·5
$\bar{7}$	+ 57	+ 50·5	+ 73	+56	+16	+31	—	+33	+26	+26·5	—
$\bar{8}$	—	+ 40·5	+ 91	+44·5	+67	−16·5	−12·5	—	+10	+11	—
$\bar{9}$	+ 17·5	+ 28	+ 35	—	+66·5	+40·5	—	−10	+33	—	—
$\overline{10}$	+ 34	+ 17	+ 38·5	+26·5	—	+32·5	+37·5	+24	+30	+16	+12·5
$\overline{11}$	+ 16	− 11·5	+ 26·5	+26	−14	+30·5	+25·5	—	+32·5	+16·5	—
$\overline{12}$	—	—	—	+22	—	—	+33	—	+14·5	—	—
$\overline{13}$	—	+ 41	—	—	+46	+38	+18	+15·5	+11·5	—	—
$\overline{14}$	—	—	—	—	—	+24·5	+36	+13·5	—	—	—

There are fewer absent reflections than in the metal-free compound. The great majority of those present are of positive sign, and the remaining negative values are all relatively small. This is due to the positive contribution made by the two nickel atoms to each reflection. Calculation shows that if the atomic number of the central metal atom were increased to about 60, all the structure factors would be of positive sign. This result suggests a new method of direct analysis, *viz.*, by introducing an element at a known point in the structure of sufficient scattering power to " swamp " all the reflections. In a centro-symmetrical structure of the present type, the effect would be to convert all the structure factors to positive sign, and a direct Fourier analysis could be carried out. We hope to apply this method in a later investigation to find the orientation of the platinum phthalocyanine molecule in the crystal, which is not isomorphous with the other members of this series.

FIG. 1.

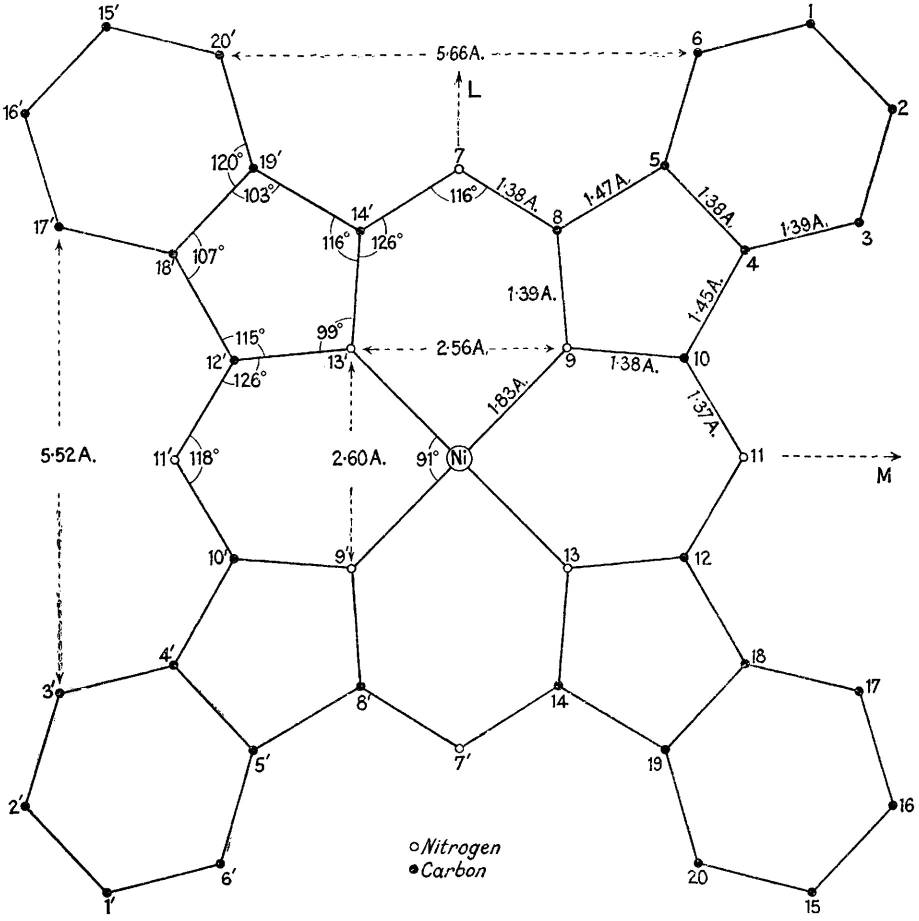
Projection of nickel phthalocyanine along the b *axis, which makes an angle of* 44·2° *with the molecular plane. Each contour line represents a density increment of one electron per* A.^{2}, *except on the central nickel atom, where the increment is five electrons per* A.^{2} *for each line. The one-electron line is dotted.*



The result of the double Fourier synthesis for nickel phthalocyanine, with the figures of Table I as coefficients, is shown by the contoured map in Fig. 1 (which should be compared with Fig. 2 of the previous paper, *loc. cit.*, p. 1201). The resolution of the various atoms is quite equal to that obtained with free phthalocyanine, and the whole structure is closely similar, apart from the central nickel atom. On the nickel atom the contour levels, after the dotted one-electron line, are drawn at intervals of 5 electrons per A.^{2}, and the peak value of the density at the centre is 39 electrons per A.^{2}. This extreme peak, however, appears to have very little distorting effect on the surrounding structure.

FIG. 2.

Dimensions of the nickel phthalocyanine molecule.



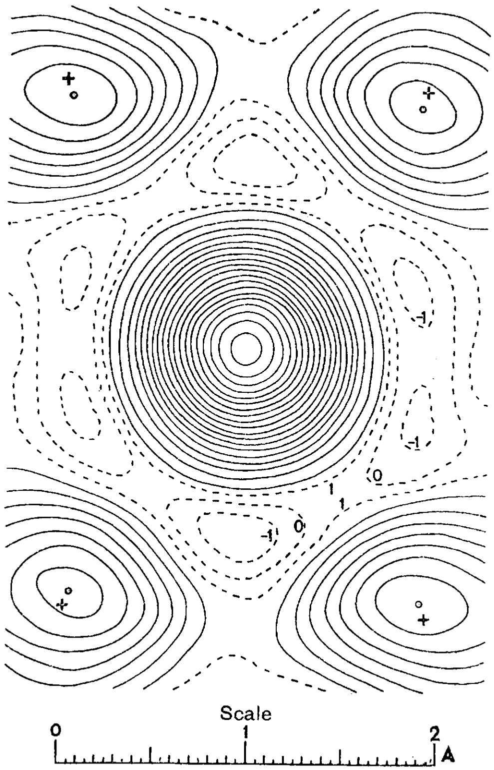
The map can be measured, and the orientation of the molecule in the crystal calculated, in a manner similar to that described for free phthalocyanine. Details are given in the experimental section. It is found that the molecule is planar and the orientation is almost identical with that of free phthalocyanine, the molecular plane making an angle of 44·2° with the projection plane, (010).

Discussion of the Structure.—From the molecular co-ordinates in Table III a normal projection of the molecule can be made, and this is shown in Fig. 2. The benzene rings appear as sensibly regular plane hexagons, the length of the sides deviating by not more than 0·04 A. from the mean value of 1·39 A. which was assumed in calculating the orientation of the molecule. These rings are connected to the inner carbon–nitrogen nucleus by C–C links of length 1·47 and 1·45 A. The corresponding links in free phthalocyanine gave the uniform value of 1·49 A. The small contraction found for nickel phthalocyanine is practically within the limits of error (about 0·03 A.) and we should not attach much importance to this result.

The structure of the inner nucleus, however, shows certain changes compared with free phthalocyanine which, although not of large magnitude, are yet definitely beyond the limits of probable error which would arise from deficiencies in the experimental work or in the construction of the map. The largest of these is a shift of about 0·09 A. of each of the four *iso*indole nitrogen atoms towards the nickel atom to which they are bound by covalent or co-ordinate links. The movement is effected largely by a readjustment of the angles around the 16-membered C–N ring (compare with Fig. 3 of the previous paper). In particular, the angles at the apex (9,13) of the *iso*indole pentagons have decreased from 108° to 99°, while the side angles (8, 10, 12, 14) have increased by 4—6°.

FIG. 3.

Enlargement of central portion of molecule.



As a result of the inward displacement of the *iso*indole nitrogen atoms, their distance from the centre of the nickel atom is now only 1·83 A., compared with a corresponding value of 1·92 A. in the metal-free compound, measured from the nitrogen atoms to the centre of the molecule. It is interesting to note that this nickel–nitrogen distance of 1·83 A. is very close to the sum of the radii of neutral nickel (1·24 A.) and doubly-linked nitrogen (0·61 A.). When a larger metal atom, such as platinum (radius 1·38 A.), is substituted in the phthalocyanine molecule, it is probable that the inward displacement of the nitrogen atoms observed in the present structure will be diminished or even reversed (cf. Barrett, Dent, and Linstead, J., 1936, 1719).

In addition to these changes there is an interesting alteration in the dimensions of the C–N links in the nucleus itself. For free phthalocyanine these had the practically constant value of 1·33—1·34 A. In the present structure, the links 9—8 and 9—10, forming two sides of the *iso*indole pentagon, have increased in length to 1·38—1·39 A., a result which might to some extent have been anticipated in view of the strong covalent attachment of atom 9 to the central nickel atom. But the remaining links of the 16-membered ring, 8—7 and 10—11, although situated far from the nickel atom, have also increased in length to 1·38 and 1·37 A.; the net result being that *all the* C–N *links of the nucleus remain of practically equal length*, although about 0·04 A. longer than in free phthalocyanine.

It should be emphasised that this change in interatomic distance within the nucleus is of small order, and not much above the limit of uncertainty imposed by the incomplete resolution of the various atoms. The inward shift of the *iso*indole nitrogen atoms, amounting to 0·09 A., appears to be quite definite, but even here there are disturbing factors. These can best be studied by reference to Fig. 3, which gives an enlarged projection of the central portion of the molecule. The contour levels of the nickel atom are here drawn for density increments of 2 electrons per A.^{2}, the 1, 0, and — 1 levels are dotted, and all the other lines are at unit intervals. The roundness of the nickel atom indicates that there are no serious errors in the experimental work or in the calculations. The contours deviate very slightly from true circles, although there is a small elongation in the direction of the *c* axis, a fact which may indicate a preferred direction in the thermal movements of the atom.

The four surrounding *iso*indole nitrogen atoms are shown at the corners of the diagram and the positions of the centres, obtained by averaging the four atoms and from other considerations, are indicated by small circles. The corresponding centres obtained from free phthalocyanine are shown by crosses. The inward shift of the atoms seems to be quite definite, and it might even be slightly greater than the amount we have given. There is, however, the difficulty of allowing for certain spurious undulations which may surround the nickel atom, due to the Fourier series being incomplete. Six small troughs will be observed, where the density drops to from — 1 to — 1·5 (as against a peak value at the centre of the nickel atom of 39). Further out, on a circle which will approximately pass through the *iso*indole nitrogen atoms, we might expect similar spurious *peaks*, and two such effects can be observed in Fig. 1, in line with the nitrogen atoms 11 and 11′. These effects, if present on the *iso*indole nitrogen atoms, might give a false impression of the positions of their centres, but we do not think they would explain the inward shift of the atoms that has been found. More abrupt distortions of the contour levels might be expected if such false detail were present on these atoms.

It is interesting to note that quite well-defined bridges exist in the direction of the covalent links connecting the nickel atom to the four nitrogen atoms (Fig. 3). The density in these regions is quite small, being only 0·5—0·7 electron per A.^{2}, but the result seems fairly definite as the bridges stand out above the adjacent negative portions.

In free phthalocyanine (J., 1936, 1205) it was shown that the molecule was slightly distorted from true tetragonal symmetry in a systematic manner which could be explained qualitatively by assuming that the distorting forces acted between the pairs of *iso*indole nitrogen atoms 9, 13′ and 13, 9′. To explain these forces, hydrogen-bond formation was assumed between the nitrogen atoms. We might expect that in nickel phthalocyanine these distortions would disappear and the molecule become truly tetragonal, owing to the more symmetrical distribution of the binding forces towards the central nickel atom.

The symmetry of the molecule can be tested in the same way as for free phthalocyanine, *viz.*, by comparing the lengths of horizontal and vertical lines connecting corresponding pairs of atoms, which would be equidistant if the molecules were exactly tetragonal. The measurements for nickel phthalocyanine are given (in A.) in Table II, with the differences in the lengths of corresponding lines, which give a measure of the departure from true tetragonal symmetry. The differences found for the free phthalocyanine molecule are also given for comparison.

TABLE II.

Test of Symmetry.

		Differences.	
Horizontal lines.	Vertical lines.	Nickel phthalocyanine.	Free phthalocyanine.
8, 14′ = 2·34	10, 12 = 2·36	−0·02	−0·03
9, 13′ = 2·56	9, 13 = 2·60	−0·04	−0·11
10, 12′ = 5·32	8, 14 = 5·38	−0·06	−0·14
11, 11′ = 6·72	7, 7′ = 6·84	−0·12	−0·22
1, 15′ = 8·36	2, 16 = 8·18	0·18	0·24
6, 20′ = 5·66	3, 17 = 5·52	0·14	0·19
2, 16′ = 10·30	1, 15 = 10·22	0·08	0·20
5, 19′ = 4·88	4, 18 = 4·87	0·01	0·08
3, 17′ = 9·47	6, 20 = 9·56	−0·09	0·08
4, 18′ = 6·77	5, 19 = 6·88	−0·11	0·03

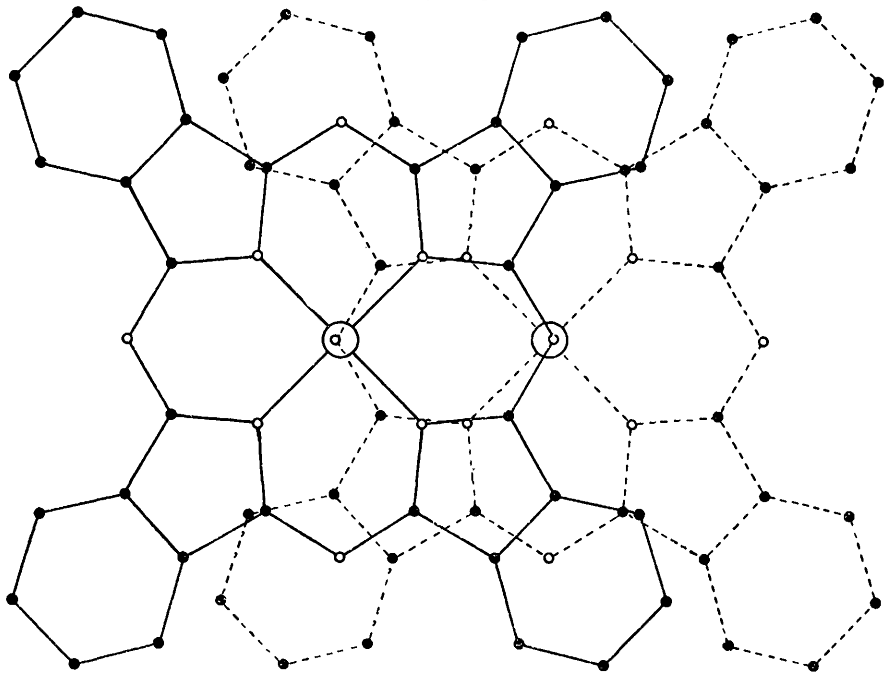
The differences are all less in nickel phthalocyanine, except the last two, which have changed in sign. The molecule has thus become more truly tetragonal with the insertion of the nickel atom, a fact which lends some support to the theory of internal hydrogen bonds previously discussed. But the remaining distortions are hard to explain. The molecule appears to retain a slight deformation of the same type as found in the free compound.

With regard to the minimum intermolecular distances and the arrangement of molecules in the crystal, the calculations and diagrams given for free phthalocyanine (*loc. cit.*, p. 1207) apply to the nickel derivative with sufficient accuracy for most purposes. The perpendicular distance between the planes of parallel molecules situated at either end of the b axis translation is 3·38 A., and the normal projection of one of these molecules in the plane of the other is shown in Fig. 4. The dotted lines connect the atoms of one molecule whose plane lies 3·38 A. beneath the other. It is seen that the outer nitrogen atom of one molecule comes almost exactly over the nickel atom of the other molecule. The distance between the two atoms is thus only 3·38 A., which is practically equal to the closest distance of intermolecular approach in the whole structure (compare data for free phthalocyanine).

In the crystal, therefore, the nickel atom is surrounded by six nitrogen atoms. Four of these lie at the corners of a square, 1·83 A. from the nickel atom, and bound to it by covalent (or co-ordinate) links. The other two lie vertically above and below the nickel atom, at a distance of 3·38 A. It can be seen from Fig. 4 that none of the other atoms in the molecule comes exactly over another in this manner. In fact, there is a distinct tendency for the atoms of the underlying molecule to be found in the gaps between the atoms of the upper molecule, a fact which probably governs the orientation assumed by the molecules in the crystal.

FIG. 4.

Normal projection of two parallel molecules.



EXPERIMENTAL.

Fourier Analysis and Orientation of the Molecule.—The measurement of intensities and examples of the determination of phase constants for nickel phthalocyanine have already been described (*loc. cit.*, p. 1196). In preparing the contour map shown in Fig. 1, the electron-density series for the ($h0l$) zone was summed at 1800 different points on the asymmetric unit, the axial sub-divisions being the same as those employed for free phthalocyanine. Measurements from the map are referred to the molecular axes L and M (Fig. 2). The 19 lines connecting pairs of atoms in the L direction, (7, 7′), (8, 14), (9, 13), etc., are all found to be parallel to within ± 0·5°, and their mean direction makes an angle of 69·45° with the a axis (η_L). Similarly, the 19 lines connecting atoms in the M direction, (11, 11′), (10, 12′), (9, 13′), etc., are parallel to within ± 0·35°, and their mean direction makes an angle of $-$ 22·4° with the a axis (η_M). For free phthalocyanine we found $\eta_L = 69{\cdot}3°$ and $\eta_M = -22{\cdot}9°$. The difference of 0·5° in η_M is probably significant, as we should estimate the error in the mean value for the 19 lines at 0·1° to 0·2°.

The inclination of the M molecular axis to the b axis of the crystal (ψ_M) can be calculated in the manner previously described, by making use of the four benzene rings as " indicators." The results are as follows :

$$\text{Ring } 1 \ldots 4,\ \psi_M = 46{\cdot}6^\circ. \qquad \text{Ring } 15 \ldots 18,\ \psi_M = 45{\cdot}2^\circ.$$

$$\text{Ring } 1' \ldots 4',\ \psi_M = 45{\cdot}9^\circ. \qquad \text{Ring } 15' \ldots 18',\ \psi_M = 45{\cdot}8^\circ.$$

$$\text{Mean } \psi_M = 45{\cdot}9^\circ.$$

The mean result is probably accurate to within 1°, and it happens to be identical with ψ_M for free phthalocyanine. From these figures, and the six equations given in the previous paper, the complete orientation of the molecule in the crystal can be calculated, with the following results :

$$\chi_L = 69{\cdot}5^\circ \quad \cos\chi_L = 0{\cdot}3508 \qquad \chi_M = 48{\cdot}4^\circ \quad \cos\chi_M = 0{\cdot}6638$$

$$\psi_L = 88{\cdot}1^\circ \quad \cos\psi_L = 0{\cdot}0335 \qquad \psi_M = 45{\cdot}9^\circ \quad \cos\psi_M = 0{\cdot}6960$$

$$\omega_L = 20{\cdot}6^\circ \quad \cos\omega_L = 0{\cdot}9358 \qquad \omega_M = 105{\cdot}9^\circ \quad \cos\omega_M = -\,0{\cdot}2737$$

$$\chi_N = 131{\cdot}3^\circ \quad \cos\chi_N = -\,0{\cdot}6605$$

$$\psi_N = 44{\cdot}2^\circ \quad \cos\psi_N = 0{\cdot}7173$$

$$\omega_N = 77{\cdot}2^\circ \quad \cos\omega_N = 0{\cdot}2223$$

Molecular Dimensions and Co-ordinates.—The positions of the atoms obtained by measurement of the contour map are given in Table III. Individual measurements of the co-ordinates taken parallel to the L and the M axis are first given (l and m) and in the last two columns the mean value is multiplied by the sine of the inclination of the molecular axis to the b crystal axis, along which the projection is made. This gives the actual molecular co-ordinates, L and M, from which the dimensions and angles in Fig. 2 are calculated. The accuracy varies somewhat in different parts of the projection; *e.g.*, the M co-ordinates of atoms 9 and 10 are less certain than their L co-ordinates. But in general the error should not be greater than 0·02—0·04 A.

TABLE III.

Co-ordinates with Respect to Molecular Axes.

			Mean value, A.	
Atoms.	l measured, A.	m measured, A.	$L(l \sin\psi_L)$.	$M(m \sin\psi_M)$.
1, 15	5·12, 5·11	2·98, 3·02	±5·11	4·18
2, 16	4·11, 4·08	3·70, 3·70	±4·09	5·15
3, 17	2·78, 2·74	3·42, 3·38	±2·76	$4{\cdot}73_5$
4, 18	2·45, 2·42	2·45, 2·41	$\pm 2{\cdot}43_5$	$3{\cdot}38_5$
5, 19	3·45, 3·43	1·75, 1·75	±3·44	2·44
6, 20	4·78, 4·78	2·02, 2·05	±4·78	2·83
7	3·42	0	±3·42	0
8, 14	2·69, 2·69	0·85, 0·83	±2·69	1·17
9, 13	1·31, 1·29	0·92, 0·92	±1·30	1·28
10, 12	1·18, 1·18	1·91, 1·91	±1·18	2·66
11	0	$2{\cdot}41_5$	0	3·36

The co-ordinates of the atoms referred to the monoclinic crystal axes can be obtained by combining the molecular co-ordinates with the orientation direction cosines given above, or by direct measurement from the Fourier projection. The results are given in Table IV, and these values are used in the structure factor calculations.

Calculation of Structure Factors. Electron Counts.—From the crystal co-ordinates of free phthalocyanine (J., 1936, 1204) and the formulæ for the space group $P2_1/a$ (cf. " International Tables for the Determination of Crystal Structure," Vol. 1, p. 102) the geometrical structure factors of all the reflections of free phthalocyanine have been calculated. The signs of the factors so obtained are found to agree in every case with the direct experimental determinations of the phase constants upon which this analysis has been based, except for the very weak (16, 0, 1) which has changed from — to +. This single change can have no significant effect on the projection.

The proper structure factors, F, which express the ratio of the amplitude actually given by a reflection to the amplitude which would be given if the contents of the unit cell were replaced by a single electron, were obtained from the relation $F = Sf$, where S is the geometrical structure factor, and f is a function which expresses the average reflecting power of the atoms in the crystal, in terms of θ, the angle of incidence of the rays. As 64 out of the 80 atoms (without counting hydrogen) in the unit cell of phthalocyanine are carbon, we have employed the f-values for typical organic hydrocarbons (*Proc. Roy. Soc., A*, 1935, **150**, 110), increasing the contributions

TABLE IV.

Co-ordinates with Respect to Monoclinic Crystal Axes. Centre of Symmetry as Origin.

Atom.	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
Ni	0	0°	0	0°	0	0°
1 CH	6·83	123·6	3·08	235·3	4·29	103·6
2 CH	6·36	115·0	3·72	284·4	2·85	68·9
3 CH	4·91	88·9	3·39	258·9	1·51	36·6
4 C	3·94	71·3	2·44	186·2	1·59	38·5
5 C	4·41	79·8	1·81	138·5	3·01	72·7
6 CH	5·86	105·9	2·13	162·9	4·36	105·3
7 N	3·19	57·7	0·12	8·8	3·77	91·1
8 C	3·09	55·9	0·90	69·1	2·59	62·6
9 N	1·85	33·4	0·94	71·6	1·02	24·6
10 C	2·41	43·7	1·89	144·5	0·44	10·7
11 N	1·66	30·0	2·34	178·8	−1·08	−26·2
12 C	0·21	3·8	1·81	138·5	−2·16	−52·2
13 N	−0·58	−10·5	0·85	64·8	−1·85	−44·6
14 C	−1·93	−35·0	0·72	55·3	−3·34	−80·8
15 CH	−2·71	−49·0	2·74	209·1	−6·98	−168·7
16 CH	−1·28	−23·1	3·45	263·5	−6·17	−149·1
17 CH	−0·24	−4·3	3·20	244·8	−4·57	−110·4
18 C	−0·60	−10·9	2·27	173·8	−3·78	−91·2
19 C	−2·01	−36·3	1·58	120·9	−4·58	−110·6
20 CH	−3·07	−55·4	1·81	138·5	−6·18	−149·4

of the nitrogen atoms relative to the carbon atoms by 20%, which is rather more than the ratio suggested by their atomic numbers.

The F values calculated in this manner are considerably below the measured values, and they require to be increased by a constant factor of 1·33 in order to afford the best agreements. Owing to the small size of the crystals upon which the absolute measurements were based (0·040—0·068 mg.) the *scale* of the measured F values may be in error by 5% or even more, but it does not seem possible to explain the factor 1·33 in this manner. The high measured F values are most likely due to the temperature factor for phthalocyanine (which takes account of the thermal movement of the atoms) being much less than in the case of typical organic hydrocarbons. This explanation is very probable in view of the high m. p. of the compound ($> 500°$). We have made no attempt to correct for the temperature effect in detail, but all the calculated values of F have been increased by the correlating factor of 1·33.

The measured and calculated values of F for free phthalocyanine are given in cols. 3 and 4 of Table V. In col. 5, the contributions to the structure factors of the two nickel atoms are given. These values are taken from Brindley's experimentally determined scattering curve (*Phil. Mag.*, 1936, **21**, 778), but for the $(h + k)$ odd reflections the contributions from the two nickel atoms are in opposite phase and the resultant is zero.

In the last two columns of the table the measured and calculated values of F for nickel phthalocyanine are given. The calculated values are derived from those of free phthalocyanine by the algebraic addition of the contributions from the nickel atoms. This method is sufficiently accurate to test the general agreements and the signs used in the Fourier analysis, which are all found to be correct for nickel phthalocyanine.

It is possible to make a more accurate calculation of the structure factors for nickel phthalocyanine by means of the revised co-ordinates given in Table IV of this paper; but as the displacement of the atoms, compared with free phthalocyanine, is small, differences will only be found in the higher-order reflections. A number of these structure factors with high indices have been recalculated in this manner, and it is found that on the average a small improvement in the agreements is obtained, particularly for the (16, 0, 1) and (16, 0, 2) planes. It would seem, however, that the estimated contributions of the nickel atoms (from Brindley's curve) are considerably too great for the furthest out reflections of large glancing angle (θ).

The general order of agreement between measured and calculated values of F is quite equal to that obtained for other more simple structures which have been successfully analysed. This is shown by the following figures which give the sum of the discrepancies between the measured and calculated values, expressed as a percentage of the total measured F values, for different zones in the two compounds. Absent reflections are included.

	($0kl$) Zone.	($h0l$) Zone.	($hk0$) Zone.	All reflections.
Free phthalocyanine	11·1	13·2	13·8	12·5
Ni phthalocyanine	14·0	14·4	15·1	14·2

TABLE V.

Measured and Calculated Values of the Structure Factor.

hkl.	sin θ (λ = 1·54).	$(C_{32}H_{16}N_8)H_2$.		Ni 2*F*.	$C_{32}H_{16}N_8Ni$.	
		F, meas.	*F*, calc.		*F*, meas.	*F*, calc.
200	0·092	< 5	+ 15	52	55	+ 67
400	0·183	46	− 48	47	< 6	− 1
600	0·275	38	+ 33	40	80	+ 73
800	0·367	< 9	+ 12	33	44	+ 45
10,00	0·458	11	+ 10	28	44	+ 38
12,00	0·550	16	+ 23	24	41	+ 47
14,00	0·641	<12	− 5	21	14	+ 16
16,00	0·733	15	− 21	17	<15	− 4
020	0·326	9	− 12	36	21	+ 24
040	0·652	6	+ 4	20	22	+ 24
001	0·062	78	+ 95	54	112	+149
002	0·123	85	− 95	51	37	− 44
003	0·184	39	− 41	46	10	+ 5
004	0·246	17	+ 11	42	56	+ 53
005	0·307	60	− 53	37	13	− 16
006	0·369	50	− 44	33	18	− 11
007	0·430	24	+ 25	30	57	+ 55
008	0·491	28	− 27	26	<11	− 1
009	0·553	10	− 7	24	18	+ 17
00,10	0·614	13	+ 21	22	34	+ 43
00,11	0·676	<12	+ 1	19	16	+ 20
00,12	0·737	<15	+ 6	17	<15	+ 23
011	0·174	36	− 39	0	33	− 39
012	0·204	36	− 36	0	35	− 36
013	0·246	<11	+ 16	0	<11	+ 16
014	0·295	<12	+ 1	0	<12	+ 1
015	0·348	35	+ 28	0	35	+ 28
016	0·403	38	+ 32	0	41	+ 32
017	0·460	23	+ 29	0	31	+ 29
018	0·516	<19	− 1	0	<19	− 1
019	0·576	<20	− 9	0	<20	− 9
01,10	0·636	<21	− 12	0	<21	− 12
021	0·332	<13	− 3	36	39	+ 33
022	0·349	<13	0	35	37	+ 35
023	0·375	15	+ 15	33	47	+ 48
024	0·408	48	+ 43	31	74	+ 74
025	0·448	16	− 16	29	18	+ 13
026	0·492	22	− 24	26	<16	+ 2
027	0·540	<18	− 7	24	27	+ 17
028	0·580	24	+ 27	23	59	+ 50
029	0·642	<21	− 5	21	18	+ 16
031	0·493	<17	+ 3	0	<17	+ 3
032	0·504	<17	+ 8	0	<17	+ 8
033	0·522	16	− 19	0	14	− 19
034	0·547	<17	+ 3	0	<17	+ 3
035	0·577	<17	+ 4	0	<17	+ 4
036	0·612	<17	0	0	<17	0
037	0·651	<17	+ 13	0	<17	+ 13
041	0·655	<17	+ 9	20	31	+ 29
042	0·663	<17	+ 3	20	19	+ 23
043	0·677	<20	+ 3	19	<20	+ 22
20,11	0·729	19	− 21	17	<15	− 4
20,10	0·668	43	− 43	20	20	− 23

hkl.	sin θ (λ = 1·54).	$(C_{32}H_{16}N_8)H_2$.		Ni 2F.	$C_{32}H_{16}N_8Ni$.	
		F, meas.	*F*, calc.		*F*, meas.	*F*, calc.
209	0·606	14	− 9	22	<12	+ 13
208	0·546	15	+ 13	24	39	+ 37
207	0·485	24	+ 20	27	51	+ 47
206	0·425	<10	+ 4	30	26	+ 34
205	0·364	72	− 54	34	29	− 20
204	0·305	10	+ 15	38	55	+ 53
203	0·246	13	− 16	42	31	+ 26
202	0·189	6	+ 21	46	54	+ 67
201	0·135	92	−116	50	43	− 66
$20\bar{1}$	0·079	96	+107	53	137	+160
$20\bar{2}$	0·107	17	+ 28	52	71	+ 80
$20\bar{3}$	0·156	67	+ 59	49	113	+108
$20\bar{4}$	0·212	61	− 55	44	11	− 11
$20\bar{5}$	0·270	36	+ 27	40	74	+ 67
$20\bar{6}$	0·329	< 9	+ 11	36	38	+ 47
$20\bar{7}$	0·389	21	+ 17	32	50	+ 49
$20\bar{8}$	0·449	<11	+ 9	29	41	+ 38
$20\bar{9}$	0·510	<11	+ 11	26	28	+ 37
$20,\bar{1}\bar{0}$	0·571	<12	− 10	23	17	+ 13
$20,\bar{1}\bar{1}$	0·632	38	− 37	21	11	− 16
$20,\bar{1}\bar{2}$	0·693	<12	+ 1	19	<12	+ 20
$20,\bar{1}\bar{3}$	0·757	38	+ 39	17	41	+ 56
40,10	0·729	<15	− 5	17	<15	+ 12
409	0·669	<12	+ 15	20	27	+ 35
408	0·609	<12	− 2	22	21	+ 20
407	0·550	10	+ 5	24	35	+ 29
406	0·491	35	+ 27	26	58	+ 53
405	0·434	13	− 17	29	<11	+ 12
404	0·377	66	− 61	33	28	− 28
403	0·322	< 9	+ 12	36	46	+ 48
402	0·270	< 7	+ 1	40	50	+ 41
401	0·222	12	− 16	44	29	+ 28
$40\bar{1}$	0·159	78	+ 75	48	129	+123
$40\bar{2}$	0·157	85	− 96	48	46	− 48
$40\bar{3}$	0·178	74	− 83	47	30	− 36
$40\bar{4}$	0·214	48	− 46	44	< 6	− 2
$40\bar{5}$	0·261	37	− 24	41	< 7	+ 17
$40\bar{6}$	0·312	< 8	− 5	37	33	+ 32
$40\bar{7}$	0·367	42	+ 35	33	73	+ 68
$40\bar{8}$	0·423	59	+ 58	30	91	+ 88
$40\bar{9}$	0·481	13	+ 11	27	35	+ 38
$40,\bar{1}\bar{0}$	0·539	16	+ 15	25	38	+ 40
$40,\bar{1}\bar{1}$	0·599	<12	+ 5	22	27	+ 27
$40,\bar{1}\bar{2}$	0·658	24	− 21	20	<12	− 1
$40,\bar{1}\bar{3}$	0·716	16	− 21	18	<15	− 3
609	0·737	<15	− 11	17	<15	+ 6
608	0·679	16	+ 15	19	33	+ 34
607	0·622	56	+ 53	21	78	+ 74
606	0·565	32	+ 34	23	50	+ 57
605	0·510	29	+ 21	26	49	+ 47
604	0·456	26	+ 16	28	43	+ 44
603	0·405	33	− 23	31	<10	+ 8
602	0·356	75	− 66	34	40	− 32
601	0·312	37	− 30	37	< 8	+ 7
$60\bar{1}$	0·298	40	− 40	38	< 7	− 2

TABLE V (*continued*).

		$(C_{32}H_{16}N_8)H_2$.			$C_{32}H_{16}N_8Ni$.	
hkl.	sin θ (λ = 1·54).	*F*, meas.	*F*, calc.	Ni 2*F*.	*F*, meas.	*F*, calc.
$60\bar{2}$	0·234	55	− 53	43	11	− 10
$60\bar{3}$	0·236	31	− 33	43	10	+ 10
$60\bar{4}$	0·253	< 7	+ 7	41	44	+ 48
$60\bar{5}$	0·283	16	− 21	39	25	+ 18
$60\bar{6}$	0·322	31	+ 32	36	66	+ 68
$60\bar{7}$	0·367	30	+ 18	33	56	+ 51
$60\bar{8}$	0·416	17	+ 13	30	44	+ 43
$60\bar{9}$	0·468	22	− 27	28	<11	+ 1
$60,\overline{10}$	0·522	<12	+ 2	25	26	+ 27
$60,\overline{11}$	0·578	<12	− 2	23	26	+ 21
$60,\overline{12}$	0·635	<12	+ 6	21	22	+ 27
$60,\overline{13}$	0·692	24	− 18	19	<12	+ 1
$60,\overline{14}$	0·750	27	− 22	17	<15	− 5
808	0·754	<14	− 5	17	<14	+ 12
807	0·698	<12	+ 7	19	26	+ 26
806	0·644	26	+ 30	20	42	+ 50
805	0·591	<12	− 13	23	<12	+ 10
804	0·539	19	+ 15	25	41	+ 40
803	0·490	<11	+ 3	27	29	+ 30
802	0·444	22	+ 25	29	50	+ 54
801	0·403	<10	− 4	31	31	+ 27
$80\bar{1}$	0·338	20	+ 17	35	59	+ 52
$80\bar{2}$	0·318	< 8	− 3	37	30	+ 34
$80\bar{3}$	0·310	15	+ 13	37	55	+ 50
$80\bar{4}$	0·314	9	− 7	37	38	+ 30
$80\bar{5}$	0·330	13	− 11	36	22	+ 25
$80\bar{6}$	0·355	< 9	+ 3	34	42	+ 37
$80\bar{7}$	0·389	14	− 15	32	16	+ 17
$80\bar{8}$	0·427	42	+ 43	30	67	+ 73
$80\bar{9}$	0·473	44	+ 41	27	66	+ 68
$80,\overline{10}$	0·521	15	− 19	25	<12	+ 6
$80,\overline{11}$	0·572	38	− 41	23	14	− 18
$80,\overline{12}$	0·624	<12	− 11	21	<12	+ 10
$80,\overline{13}$	0·678	27	+ 32	19	46	+ 51
$80,\overline{14}$	0·733	18	− 19	17	<15	− 2
10,07	0·775	12	− 20	16	<14	− 4
10,06	0·725	<15	+ 1	18	16	+ 19
10,05	0·674	17	− 15	19	<12	+ 4
10,04	0·625	19	− 11	21	<12	+ 10
10,03	0·578	13	+ 18	23	36	+ 41
10,02	0·534	25	− 29	25	<12	− 4
10,01	0·494	<11	+ 2	26	26	+ 28
$10,0\bar{1}$	0·429	62	+ 60	30	94	+ 90
$10,0\bar{2}$	0·406	20	+ 19	31	51	+ 50
$10,0\bar{3}$	0·392	28	+ 20	32	61	+ 52
$10,0\bar{4}$	0·388	13	+ 16	32	44	+ 48
$10,0\bar{5}$	0·393	13	− 19	32	17	+ 13
$10,0\bar{6}$	0·407	27	+ 22	31	59	+ 53
$10,0\bar{7}$	0·430	<10	+ 4	30	31	+ 34
$10,0\bar{8}$	0·460	46	− 46	28	17	− 18
$10,0\bar{9}$	0·495	15	+ 11	26	41	+ 37
$10,0,\overline{10}$	0·536	<12	+ 6	25	33	+ 31
$10,0,\overline{11}$	0·580	<12	+ 12	23	31	+ 35
$10,0,\overline{12}$	0·627	12	− 13	21	<12	+ 8
$10,0,\overline{13}$	0·676	25	+ 26	19	38	+ 45
$10,0,\overline{14}$	0·727	<15	+ 9	18	24	+ 27
12 05	0·759	<14	− 6	16	<14	+ 10
12,04	0·711	35	− 42	18	16	− 24
12,03	0·666	<12	− 6	20	21	+ 14
12,02	0·624	11	− 11	21	<12	+ 10
12,01	0·585	<12	− 6	23	22	+ 17
$12,0\bar{1}$	0·519	12	+ 13	25	38	+ 38
$12,0\bar{2}$	0·495	<11	− 5	26	22	+ 21
$12,0\bar{3}$	0·478	13	− 18	27	15	+ 9
$12,0\bar{4}$	0·467	52	+ 60	28	81	+ 88
$12,0\bar{5}$	0·465	11	+ 6	28	29	+ 34
$12,0\bar{6}$	0·471	41	− 43	27	21	− 16
$12,0\bar{7}$	0·485	31	− 27	27	<11	0
$12,0\bar{8}$	0·505	42	− 38	26	13	− 12
$12,0\bar{9}$	0·532	13	− 7	25	<12	+ 18
$12,0,\overline{10}$	0·565	10	+ 16	23	38	+ 39
$12,0,\overline{11}$	0·602	<12	+ 11	22	26	+ 33
$12,0,\overline{12}$	0·643	9	+ 12	21	33	+ 33
$12,0,\overline{13}$	0·686	<12	+ 3	19	18	+ 22
$12,0,\overline{14}$	0·732	21	+ 27	17	36	+ 44
14,03	0·756	<14	+ 13	17	18	+ 30
14,02	0·714	14	+ 16	18	18	+ 34
14,01	0·676	33	− 37	19	15	− 18
$14,0\bar{1}$	0·611	<12	− 1	22	25	+ 21
$14,0\bar{2}$	0·585	<12	+ 3	23	25	+ 26
$14,0\bar{3}$	0·565	29	− 28	23	<12	− 5
$14,0\bar{4}$	0·551	10	− 11	24	15	+ 13
$14,0\bar{5}$	0·543	11	+ 11	24	35	+ 35
$14,0\bar{6}$	0·543	16	+ 11	24	40	+ 35
$14,0\bar{7}$	0·549	9	+ 11	24	33	+ 35
$14,0\bar{8}$	0·562	22	− 20	24	<12	+ 4
$14,0\bar{9}$	0·582	37	− 35	23	10	− 12
$14,0,\overline{10}$	0·606	<12	+ 7	22	24	+ 29
$14,0,\overline{11}$	0·637	<12	− 9	21	<12	+ 12
$14,0,\overline{12}$	0·671	<12	− 1	20	<12	+ 19
$14,0,\overline{13}$	0·709	<16	+ 5	18	16	+ 23
$14,0,\overline{14}$	0·749	<15	+ 9	17	13	+ 26
16,02	0·805	16	+ 25	15	24	+ 40
16,01	0·767	10	+ 10	16	<14	+ 26
$16,0\bar{1}$	0·702	13	− 11	18	<16	+ 7
$16,0\bar{2}$	0·675	10	+ 15	19	29	+ 34
$16,0\bar{3}$	0·653	<12	+ 7	20	17	+ 27
$16,0\bar{4}$	0·637	29	− 31	21	<12	− 10
$16,0\bar{5}$	0·625	<12	− 2	21	17	+ 19
$16,0\bar{6}$	0·620	<12	+ 10	21	31	+ 31
$16,0\bar{7}$	0·621	<12	+ 7	21	26	+ 28
$16,0\bar{8}$	0·628	<12	− 6	21	10	+ 15
$16,0\bar{9}$	0·641	9	+ 10	21	33	+ 31
$16,0,\overline{10}$	0·659	10	+ 7	20	30	+ 27
$16,0,\overline{11}$	0·682	10	+ 11	19	32	+ 30
$16,0,\overline{12}$	0·710	<16	+ 4	18	15	+ 22
$16,0,\overline{13}$	0·741	<15	+ 5	17	12	+ 22
$18,0\bar{2}$	0·766	27	− 31	16	<14	− 15
$18,0\bar{3}$	0·742	<15	+ 1	17	12	+ 18
$18,0\bar{4}$	0·724	26	+ 27	18	38	+ 45
$18,0\bar{5}$	0·710	27	+ 29	18	36	+ 47
$18,0\bar{6}$	0·702	<16	+ 1	18	14	+ 19
$18,0\bar{7}$	0·697	<16	+ 11	19	27	+ 30
$18,0\bar{8}$	0·699	<16	+ 2	19	11	+ 21

TABLE V (*continued*).

		$(C_{32}H_{16}N_8)H_2$.			$C_{32}H_{16}N_8Ni$.	
hkl.	sin θ ($\lambda =$ 1·54).	F, meas.	F, calc.	Ni $2F$.	F, meas.	F, calc.
$18,0\bar{9}$	0·706	<16	− 5	18	<16	+ 13
$18,0,\bar{1}\bar{0}$	0·718	<15	+ 5	18	16	+ 23
$18,0,\bar{1}\bar{1}$	0·736	<15	+ 8	17	16	+ 25
$20,0\bar{6}$	0·785	<14	+ 12	16	12	+ 28
$20,0\bar{7}$	0·778	<14	+ 9	16	<14	+ 25
$20,0\bar{8}$	0·775	<14	− 1	16	<14	+ 15
$20,0\bar{9}$	0·777	14	− 18	16	13	− 2
$20,0,\bar{1}\bar{0}$	0·785	<14	+ 15	16	12	+ 31
110	0·169	66	− 71	48	9	− 23
210	0·187	53	+ 63	0	44	+ 63
310	0·213	19	− 19	44	20	+ 25
410	0·245	21	− 23	0	14	− 23
510	0·281	< 7	− 4	39	38	+ 35
610	0·320	10	− 4	0	<11	− 4
710	0·360	< 8	+ 1	34	37	+ 35
810	0·401	12	+ 16	0	<14	+ 16
910	0·443	28	− 25	29	<15	+ 4
10,10	0·486	16	− 12	0	<16	− 12
11,10	0·529	<11	+ 3	25	29	+ 28
12,10	0·573	<11	− 11	0	<19	− 11
13,10	0·618	<13	0	22	<21	+ 22
14,10	0·661	<14	+ 9	0	<23	+ 9
15,10	0·706	<14	− 12	18	<23	+ 6
120	0·329	< 7	− 5	0	<13	− 5
220	0·339	11	− 19	35	13	+ 16
320	0·354	< 8	− 7	0	<13	− 7
420	0·374	< 8	− 1	33	23	+ 32
520	0·399	32	− 37	0	26	− 37
620	0·427	14	+ 17	30	52	+ 47
720	0·457	<10	0	0	<16	0
820	0·491	10	− 15	26	<16	+ 11
920	0·526	<11	− 5	0	<18	− 5
10,20	0·562	<11	+ 9	24	15	+ 33
11,20	0·600	36	− 33	0	24	− 33
12,20	0·639	12	− 17	21	<19	+ 4
13,20	0·679	<14	+ 7	0	<23	+ 7
14,20	0·719	17	+ 13	18	<23	+ 31
130	0·491	14	− 12	26	<18	+ 14
230	0·497	<11	− 8	0	<18	− 8
330	0·508	<11	− 4	26	13	+ 22
430	0·522	<11	− 1	0	<18	− 1
530	0·540	13	+ 20	24	31	+ 44
630	0·561	<11	− 11	0	<19	− 11
730	0·585	<12	+ 7	23	21	+ 30
830	0·611	<13	+ 5	0	<21	+ 5
930	0·640	<14	+ 8	21	<23	+ 29
10,30	0·670	22	+ 20	0	<23	+ 20
11,30	0·702	<14	+ 4	18	<23	+ 22
140	0·653	11	− 12	0	<20	− 12
240	0·659	<12	− 4	20	<20	+ 16
340	0·666	<12	− 1	0	<20	− 1
440	0·677	<14	+ 9	19	<23	+ 28
540	0·691	<14	+ 11	0	<23	+ 11
640	0·707	<14	− 9	18	<23	+ 9
740	0·726	16	+ 24	0	<23	+ 24

The measured structure factors of the two strongest reflections for nickel phthalocyanine, the (001) and ($20\bar{1}$), are considerably less than the calculated values, probably owing to an extinction effect for which we have not been able to correct. This deficiency is shown in another way when an electron count is made for the nickel atom. When the density is integrated over the area of the nickel atom, we find 25·6 electrons instead of 28 as required by the atomic number of nickel. But if the amplitudes of the component terms in the Fourier series due to the (001) and ($20\bar{1}$) reflections are increased to the calculated values, the electron count gives a result of 26·9. The remaining deficiency of one electron is probably due to the omission of weak reflections lying beyond our experimental limits, the majority of which will make positive contributions, and so add to the density on the nickel atom.

An electron count has also been carried out on the nitrogen atom 11, which is one of the best resolved atoms in the structure, and sufficiently clear of its neighbours to give accurate results. The value obtained is 7·0 electrons.

SUMMARY.

The structure of nickel phthalocyanine has been determined by a double Fourier synthesis of the *X*-ray crystal data for the (*h*0*l*) zone of reflections, employing absolute measurements of intensities and a direct determination of the phase constants by comparisons with free phthalocyanine. The results are expressed by a contoured electron-density map of the molecule in which every atom is separately resolved. The 60 parameters of the structure are determined to within 0·02—0·04 A. The molecule is planar, and its orientation in the crystal is practically identical with that of free phthalocyanine. The structure of the molecule is also closely similar to that of free phthalocyanine, but there is a definite inward shift, amounting to about 0·09 A., of each of the four *iso*indole nitrogen atoms towards the central nickel atom to which they are bound by covalent links. The C–N interatomic distance of the inner nucleus is 1·38 A., slightly greater than the value found for free

phthalocyanine. The molecule is more nearly tetragonal than free phthalocyanine, but a small deformation still exists.

The structures assigned to nickel phthalocyanine and free phthalocyanine have been verified by the calculation of all the structure factors from the co-ordinates of the atoms. Some electron counts are given.

In conclusion, we wish to thank Sir William Bragg and the Managers of the Royal Institution for their continued interest in this work.

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