255. *An X-Ray Study of the Phthalocyanines. Part II. Quantitative Structure Determination of the Metal-free Compound.*

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PRELIMINARY data on the crystal structure of some of the phthalocyanines have already been given (J., 1935, 615). These compounds (see Linstead, J., 1934, 1016) form an isomorphous series of remarkably stable monoclinic crystals. The present paper gives the results of a quantitative determination of the structure of free phthalocyanine, $C_{32}H_{18}N_8$, space group C^5_{2h} ($P2_1/a$), $a = 19{\cdot}85$, $b = 4{\cdot}72$, $c = 14{\cdot}8$ A., $\beta = 122{\cdot}25°$, which has two centro-symmetrical molecules per unit cell of volume 1173 A.^{3}; d (found) $= 1{\cdot}44$; (calc.) $= 1{\cdot}445$, $M = 514$, $F(000) = 532$.

It is well known that the direct application of the *X*-ray method of analysis is severely limited in the general case by the ambiguity of the phase constant. It is possible to make absolute measurements of the intensities of the *X*-ray crystal reflections, and from these values to calculate the magnitudes of the structure amplitude factors (F). But the complete expression of F, as it occurs in the Fourier series representing the electron density at any point in the crystal lattice, is a complex quantity characterised by an amplitude and a phase constant. As the *X*-ray crystal reflections are recorded separately, at different times and with the crystal in different positions, all information regarding the relative values of the phase constants is necessarily lost in making the experiment with a single crystal. However, it is usually possible to proceed with the analysis by methods of trial, making use of previous knowledge of the scattering power of atoms and the probable distances between them. The application of the Fourier synthesis then leads to a refinement of the preliminary results, and by a method of successive approximation is equivalent in the end to a direct determination of the interatomic distances. The analyses already carried out in this way for organic structures (*Proc. Roy. Soc.*, 1933, *A*, **140**, 79; 1935, *A*, **150**, 348; etc.) are thus to some extent unsatisfactory, not because they are lacking in truth, but because of the rather indirect manner by which the results have been obtained.

It is remarkable that the complex phthalocyanine molecule, governed by 60 independent parameters for the carbon and nitrogen atoms alone, should be the first organic structure to yield to an absolutely direct *X*-ray analysis which does not even involve any assumptions regarding the existence of discrete atoms in the molecule. We do, however, require some knowledge of the properties of the metal atom in the phthalocyanine derivatives; *e.g.*, we require to know its atomic number and its atomic weight approximately, and we have to assume that most of its electrons are concentrated in a space which is quite small compared to the size of the whole molecule. One other assumption, which follows from the isomorphism of these compounds, is necessary. If the dimensions of the unit cells of two related members of the series are very closely similar, we assume a corresponding similarity in the structures contained within these cells, not necessarily in detail, but in broad outline, especially in the overall dimensions of the related molecules. The remainder of the analysis is perfectly direct, because both the amplitudes and the phase constants of the component terms in the Fourier series for the electron density can be determined from a double series of absolute intensity measurements from the compound with and without a metal atom present. This applies generally to the ($h0l$) zone, which gives by far the most important projection of the structure, and with certain exceptions, noted in a later section, to the other zones.

The structures possess centres of symmetry. The phase constants are thus limited to 0 or π; *i.e.*, either a peak or a trough of each component sinusoidal distribution of density in the structure must coincide with the centre of symmetry. But these two possible values of the phase constant still give 2^n possible solutions of the structure, where n is the number of measurable reflections.

Each *X*-ray reflection is the resultant of the wavelets scattered by all the electrons in the structure, and the main problem is to discover the phase constant of this resultant wave. If a scattering particle is situated exactly at the centre of symmetry it will contribute a wavelet which is always a maximum (peak) to the resultant reflection. Now, we know that the metal atom enters the structure at the centre of symmetry (J., 1935, 615) and we assume that most of its scattering electrons are concentrated in a space which is small compared to the spacing of any of the reflecting planes. The metal atom alone, therefore, makes a contribution to the resultant reflection which is always a peak at the centre of symmetry. Thus by comparing the intensities of corresponding reflections with and without the metal atom in the structure, it is possible to derive the phase constants of the ($h0l$) reflections. If a reflection from the free compound corresponds in phase to a peak at the centre of symmetry, then the same reflection from the metal compound will be of greater intensity owing to the addition of the peak due to the metal atom alone, and the phase constants of both these reflections will be 0 (or positive sign). If, however, the reflection from the free compound corresponds in phase to a trough at the centre of symmetry, then the addition of the peak due to the metal atom alone will tend to fill up this trough, and the resultant reflection from the metal compound will usually be of smaller intensity, the phase constants of both reflections in this case being π (or negative sign). If the reflection from the free compound corresponds to a very small trough (weak intensity), the phase may be reversed by the addition of the metal atom. When the structure amplitudes are expressed in absolute measure there is practically no ambiguity in the principal ($h0l$) zone, and the phase constants of these reflections, numbering about 300, from phthalocyanine and its nickel derivative have been determined with certainty. Numerical details are given below.

A similar method of determining phase constants by substitution has been successful for some inorganic structures, notably the alums (Cork, *Phil. Mag.*, 1927, **4**, 688; Beevers and Lipson, *Proc. Roy. Soc.*, 1935, *A*, **148**, 664), where one element can be replaced by another of higher atomic number. In the present example the results are more direct and complete, because we can remove the metal atom entirely without appreciably disturbing the structure.

The result of the Fourier synthesis for the ($h0l$) zone of free phthalocyanine is expressed by the contour map shown in Fig. 2, which gives a projection of the structure along the b crystal axis. The electron distribution is clearly segregated into peaks which there is no difficulty in identifying as due to carbon and nitrogen atoms, the latter rising to slightly higher levels and containing more electrons. Even a rough inspection of the diagram is sufficient to show that Linstead's structure for the phthalocyanines is now established with absolute certainty. Detailed measurements from the map, and the deduction of the true orientation of the molecule in the crystal, give all the interatomic distances and valency angles with an accuracy which varies slightly in different parts of the projection, but is in general about ± 0·03 A., sufficient to determine the type of valency bond between the different atoms. The results are summarised in Fig. 3, which gives a normal projection of the molecule.

EXPERIMENTAL.

Measurement of Intensities.—To determine the structure amplitudes and phase constants by the method outlined above, it was necessary to make an exhaustive series of absolute intensity measurements from free phthalocyanine and a closely isomorphous metal derivative. Nickel phthalocyanine was chosen as the most suitable because (1) the cell measurements are practically identical with those of free phthalocyanine (J., 1935, 616); (2) well-formed single crystals can be obtained; (3) the absorption coefficient for copper radiation is comparatively low, $\mu = 16{\cdot}56$ per cm. (for free phthalocyanine the calculated absorption coefficient is $\mu = 8{\cdot}62$ per cm.); (4) the scattering power of the nickel atom, atomic number 28, for X-rays is sufficient to have a marked effect on the intensities without being great enough to swamp the reflections completely. Copper phthalocyanine is almost equally good with respect to (3) and (4), and in fact, the intensities of its reflections appear to be identical with those of nickel phthalocyanine as far as can be estimated by eye, but it is not quite so suitable with respect to (1) and (2). Cu-$K\alpha$ radiation has a wave-length near the K-absorption edges of nickel and copper. The scattering powers of these elements are thus abnormal, but this does not affect our results.

The crystals were in the form of small laths, elongated along the b axis. Most of the work on the ($h0l$) zone of free phthalocyanine was carried out on a specimen cut to 1·02 mm. in length (along the b axis), and of cross section 0·10 × 0·34 mm., weighing 0·040 mg. A slightly larger specimen of nickel phthalocyanine was employed, weighing 0·068 mg. The crystals were completely immersed in a uniform beam of filtered copper radiation, and the reflections recorded photographically by means of moving-film cameras. The strongest reflections were reduced by a known factor by use of automatic shutters on the two-crystal moving-film spectrometer (*Phil. Mag.*, 1934, **18**, 729). The range of intensities recorded was about 1600 to 1, and the measurements were carried out on the integrating photometer (Robinson, *J. Sci. Instr.*, 1933, **10**, 233) except for a few of the very weakest reflections, which had to be estimated visually on long-exposure films. Other crystal specimens of about the same size were employed to check the work, and for recording the other zones of reflections.

The measurements were put on an absolute scale by the direct determination of a few of the strongest reflections on the ionisation chamber with monochromatic rays (copper and molybdenum), and also photographically by comparisons with known standards on the two-crystal moving-film spectrometer. The various results were consistent to within about 5% in terms of F. The structure factors (F) were calculated from the integrated intensity measurements ($E\omega/I$), after correction for the absorption of the beam in the specimen, by the usual formula for the mosaic crystal. Adapted for a small crystal completely bathed in radiation, this becomes

$$F^2 = \frac{E\omega}{I} \cdot \frac{1}{\delta v} \cdot \frac{2 \sin 2\theta}{1 + \cos^2 2\theta} \cdot \frac{V^2}{\lambda^3} \left(\frac{mc^2}{e^2}\right)^2$$

δv being the volume of the specimen, and V that of the unit cell.

Owing to the shape of the specimens, the path of the X-ray beam differs when the crystals are in different reflecting positions. Correction factors were therefore calculated and applied to the comparative intensity measurements to allow for this effect. As the number of reflections is very great, this could only be done approximately, by estimating the mean path for different positions of the crystals. The results should be quite accurate for the ($h0l$) reflections, upon which the principal analysis is based, because the cross-sections of the crystals normal to the b axis are very small. For the other zones of reflections, which bring in a crystal dimension of 1 mm. or more, the corrections are less satisfactory, particularly for the nickel compound, and the resulting F values will not be so accurate; but they are quite sufficient to confirm the results of the principal analysis of the ($h0l$) zone.

Determination of Phase Constants.—The unit cells contain two molecules, and therefore, in the case of nickel phthalocyanine, two nickel atoms which are situated at centres of symmetry at (000) and ($\frac{1}{2}\frac{1}{2}0$). These atoms are always in phase for the ($h0l$) zone of reflections. If the isomorphism of phthalocyanine and its nickel derivative is sufficiently close, the structure factor of the latter can be expressed as the sum or difference of two structure factors, *viz.*, that of the nickel atoms alone and that of the remainder of the compound. It is the sum if the nickel and the remainder act together, and the difference if they do not. By examining for each reflection the sum and the difference of the factors for the compound with and without nickel, it is easy to settle which gives the factor for the two nickel atoms in the cell, because the result ought to decline continuously from the full value for two nickel atoms as the value of sin θ increases. The results are set out in Table I; F (nickel phthalocyanine) and F (free phthalocyanine) may each be either positive or negative, so that four possible combinations of these quantities are involved. But as $2F$ (nickel) must always be positive, only two of these combinations need be considered, and they are given in the table.

The scattering factor for the nickel atom has recently been determined experimentally by Brindley (*Phil. Mag.*, 1935, **20**, 865; 1936, **21**, 778), but for our purpose only the very roughest knowledge of this factor is required. In fact, it is sufficient to know that the values begin at 56 (twice the atomic number) for zero glancing angle and diminish continuously as the angle increases until, for sin θ(Cu-$K\alpha$) = 0·8, the values of $2F$ (nickel) lie between 5 and 20, in absolute units. This approximate knowledge of the scattering factor is sufficient, because the nickel contributions calculated from the difference of the two structure factors will not, in general, be the true nickel contributions. The two structures, apart from the central nickel atom, cannot be exactly identical; but they are sufficiently alike to enable the signs or phase constants to be obtained without ambiguity for nearly all the reflections, as will be seen from the examples in Table I, where the arrow indicates the combinations of sign chosen as being correct.

About 400 equations of this type are necessary to complete the ($h0l$) zones alone for the two compounds, and only a selection of the results is given. The results are represented more completely in Fig. 1, where the calculated contributions of the nickel atoms are plotted against the sine of the glancing angle of the corresponding reflection. The accepted value is indicated

TABLE I.

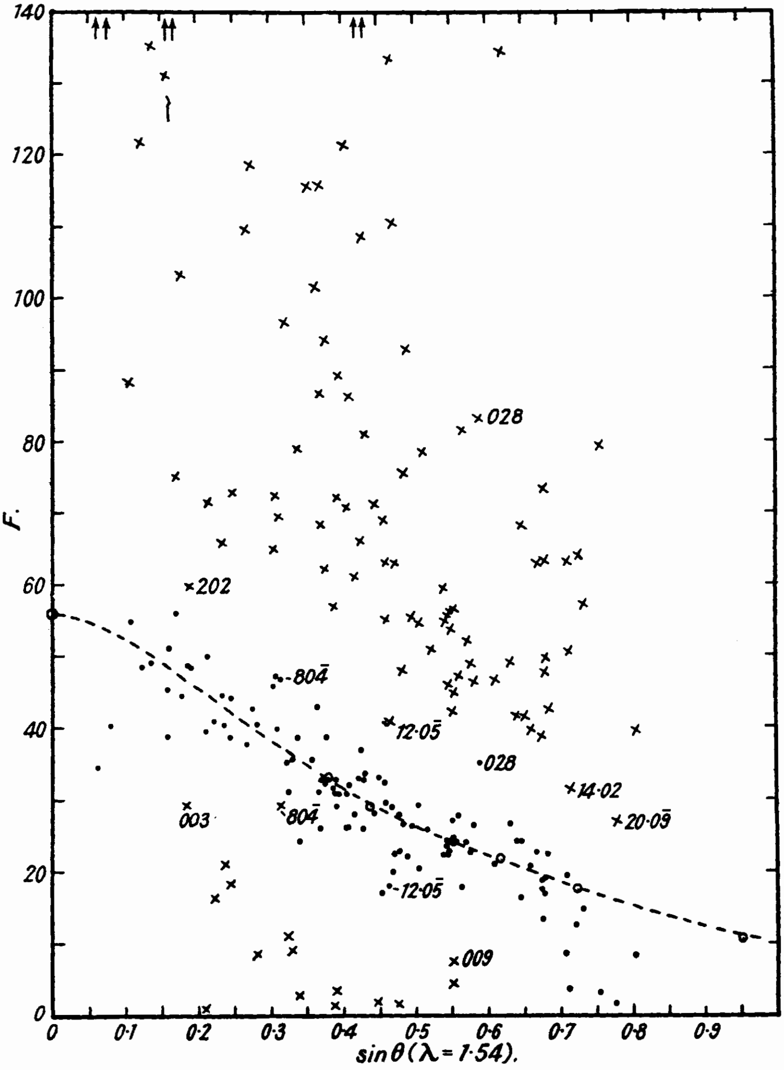
Determination of Phase Constants.

hkl.	*F* (Ni deriv.) −	*F* ($C_{32}H_{18}N_8$) =	2*F* (Ni)		sin θ.
001	(+112·0) −	(+77·6) =	34·4	←	0·062
	(+112·0) −	(−77·6) =	189·6		
$20\bar{1}$	(+136·5) −	(+96·3) =	40·2	←	0·079
	(+136·5) −	(−96·3) =	232·8		
200	(+ 55·0) −	(A < + 3·9) =	51·1		0·092
	(+ 55·0) −	(A < − 3·9) =	58·9		
$20\bar{2}$	(+ 71·4) −	(+16·6) =	54·8	←	0·107
	(+ 71·4) −	(−16·6) =	88·0		
002	(− 36·5) −	(−85·0) =	48·5	←	0·123
	(+ 36·5) −	(−85·0) =	121·5		
201	(− 43·0) −	(−92·1) =	49·1	←	0·135
	(+ 43·0) −	(−92·1) =	135·1		
$20\bar{3}$	(+112·6) −	(+67·4) =	45·2	←	0·156
	(+112·6) −	(−67·4) =	180·0		
$40\bar{2}$	(− 46·0) −	(−84·8) =	38·8	←	0·157
	(+ 46·0) −	(−84·8) =	130·8		
$40\bar{1}$	(+129·0) −	(+77·9) =	51·1	←	0·159
	(+129·0) −	(−77·9) =	206·9		
400	(A < − 5·6) −	(−45·7) =	40·1		0·183
	(A < + 5·6) −	(−45·7) =	51·3		
310	(+ 20·4) −	(−19·2) =	39·6	←	0·213
	(+ 20·4) −	(+19·2) =	1·2		
004	(+ 55·6) −	(+17·0) =	38·6	←	0·246
	(+ 55·6) −	(−17·0) =	72·6		
$20\bar{5}$	(+ 73·5) −	(+36·0) =	37·5	←	0·270
	(+ 73·5) −	(−36·0) =	109·5		
$60\bar{6}$	(+ 65·7) −	(+30·7) =	35·0	←	0·322
	(+ 65·7) −	(−30·7) =	96·4		
$40\bar{7}$	(+ 73·1) −	(+42·4) =	30·7	←	0·367
	(+ 73·1) −	(−42·4) =	115·5		
024	(+ 73·5) −	(+47·8) =	25·7	←	0·408
	(+ 73·5) −	(−47·8) =	121·3		
$12, 0\bar{3}$	(+ 14·9) −	(−13·0) =	27·9	←	0·478
	(+ 14·9) −	(+13·0) =	1·9		
804	(+ 40·7) −	(+18·6) =	22·1	←	0·539
	(+ 40·7) −	(−18·6) =	59·3		
607	(+ 78·2) −	(+56·3) =	21·9	←	0·622
	(+ 78·2) −	(−56·3) =	134·5		
$12, 0, \bar{1}\bar{4}$	(+ 36·0) −	(+21·2) =	14·8	←	0·732
	(+ 36·0) −	(−21·2) =	57·2		
16, 02	(+ 23·9) −	(+15·6) =	8·3	←	0·805
	(+ 23·9) −	(−15·6) =	39·5		

by a dot and the rejected value by a cross. Arrows at the top of the diagram indicate further rejected values that lie beyond the limits of the scale. The reflections from the (009), (202), $(80\bar{4})$, $(12,0\bar{5})$, (14,02), and $(20,0\bar{9})$ planes of free phthalocyanine are extremely faint, the structure factors varying from 6 to 14 in absolute units. It will be seen from Fig. 1 that the choice of phase constants is uncertain for these reflections, but this uncertainty only applies to free phthalocyanine. In nickel phthalocyanine the (003) and the $(20,0\bar{9})$ are also faint reflections, and the corresponding signs of the structure factors are doubtful. In general, as a sum or difference of two quantities is involved, an ambiguity only arises when one of these quantities is small. This normally corresponds to an absent reflection, but those mentioned above are on the border-line of visibility. Five of these doubtful terms have been omitted from the Fourier synthesis, but they amount to such a small fraction of the total that they can have but little effect on the final results.

The broken line and circles represent the scattering power of the nickel atoms for copper radiation taken from Brindley's revised values (*Phil. Mag.*, **1936**, **21**, 778). The dots are seen to congregate about this line. It should be noted that, although the dots depart considerably from a smooth curve, this does not necessarily indicate errors in the relative intensity measurements, but merely shows that the structures of free phthalocyanine and of nickel phthalocyanine, apart from the central metal atom, are not quite identical in detail.

FIG. 1.



The scattering contributions of the nickel atoms.

Owing to the arrangement of the centres of symmetry in the space group C_{2h}^5, the two nickel atoms at (000) and $(\frac{1}{2}\frac{1}{2}0)$ contribute waves which are in opposite phase for certain reflections in the other zones, and consequently they make no contribution to these reflections. This happens in general when $(h + k)$ is odd, as can readily be seen from the geometrical structure factors, S (cf. " International Tables for the Determination of Crystal Structure," Vol. 1, p. 102) :

$$S = 4\Sigma\cos2\pi(hx + lz)\cos2\pi ky \text{ when } (h + k) \text{ is even;}$$
$$S = 4\Sigma\sin2\pi(hx + lz)\sin2\pi ky \text{ when } (h + k) \text{ is odd.}$$

Hence when $(h + k)$ is odd the structure factors should have nearly the same values for corresponding reflections from free phthalocyanine and nickel or copper phthalocyanine, a test which gives another means of checking the isomorphism of the compounds. The experimentally determined values of F for these reflections are given in Table II, and the agreements are seen to be reasonably good. It follows, of course, that the phase constants of these reflections cannot be determined directly as in the case of the ($h0l$) zone. Fortunately, however, the latter zone is sufficient for a complete deduction of the structure, and from the results obtained, the magnitudes and phase constants of the reflections in Table II can be calculated and used to verify the main conclusions. The calculated values of the structure factors will be given in a later paper when the structure of nickel phthalocyanine is considered in detail.

TABLE II.

Comparison of (h + k) *odd reflections.*

hkl.	F, $C_{32}H_{18}N_8$.	F, Ni deriv.	hkl.	F, $C_{32}H_{18}N_8$.	F, Cu deriv.	hkl.	F, $C_{32}H_{18}N_8$.	F, Cu deriv.
011	36	33	210	53	44	11, 2, 0	36	24
012	36	35	410	21	14	13, 2, 0	$A < 14$	$A < 18$
013	$A < 11$	$A < 11$	610	10	$A < 9$	230	$A < 11$	$A < 14$
014	$A < 12$	$A < 12$	810	12	$A < 11$	430	$A < 11$	$A < 14$
015	35	35	10, 1, 0	16	$A < 13$	630	$A < 11$	$A < 15$
016	38	41	12, 1, 0	$A < 11$	$A < 15$	830	$A < 13$	$A < 17$
017	23	31	120	$A < 7$	$A < 10$	10, 3, 0	22	$A < 20$
018	$A < 19$	$A < 19$	320	$A < 8$	$A < 10$	140	11	$A < 16$
019	$A < 20$	$A < 20$	520	32	26	340	$A < 12$	$A < 16$
031	$A < 17$	$A < 17$	720	$A < 10$	$A < 13$	540	$A < 14$	$A < 18$
032	$A < 17$	$A < 17$	920	$A < 11$	$A < 14$	740	16	$A < 18$
033	16	14						

Fourier Analysis of the (h0l) *Zone, and Orientation of the Molecule.*—The values and signs of $F(h0l)$ are given in Table III. The projected density was computed from the series

$$\rho(x, z) = \frac{1}{ac \sin \beta} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(h0l) \cos 2\pi(hx/a + lz/c)$$

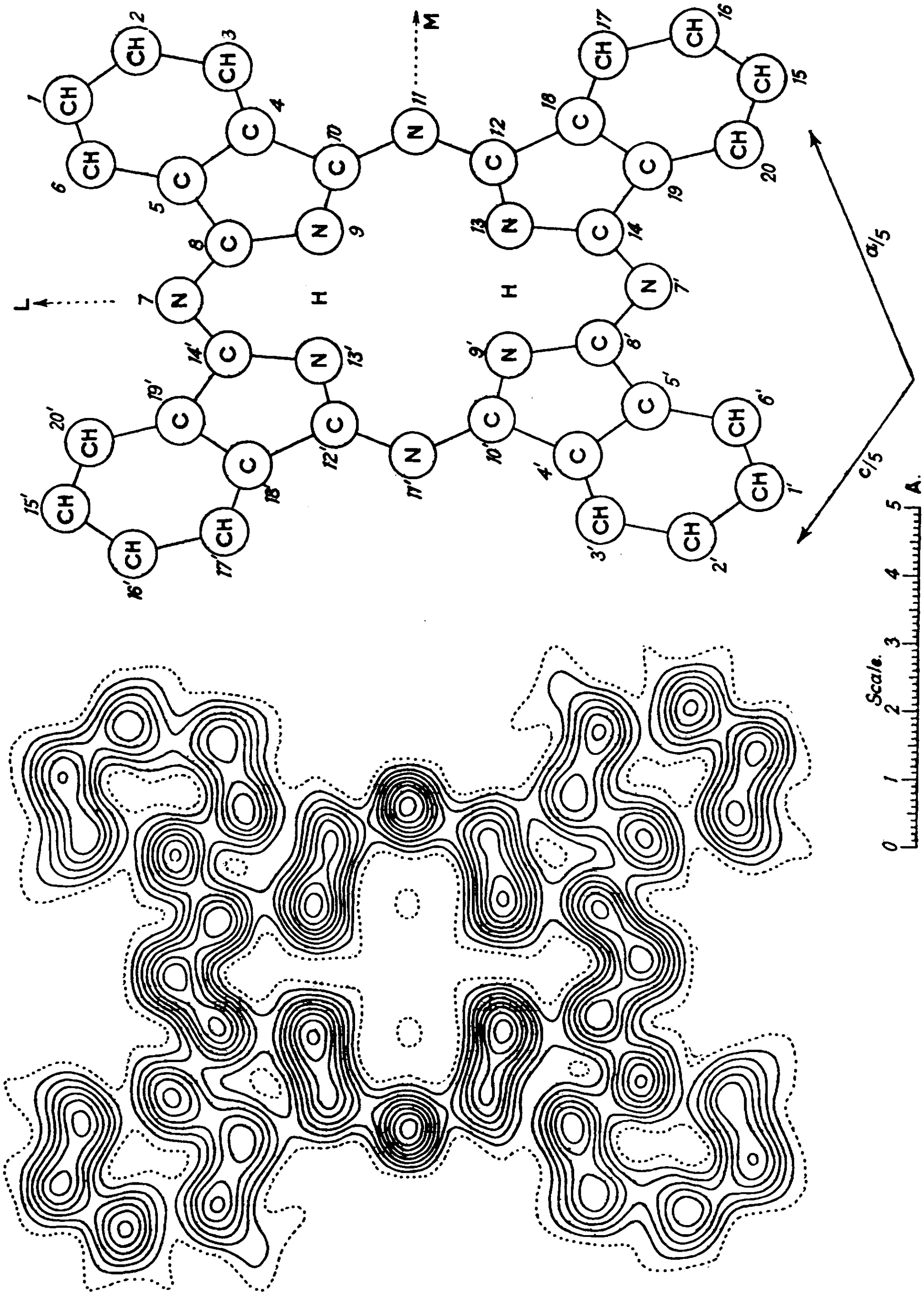
The summations were carried out at 1800 separate points on the asymmetric unit (half the molecule), the a axis being sub-divided into 120 parts (intervals of 0·165 A.) and the c axis into 60 parts (intervals of 0·247 A.). The summation totals are not reproduced, but the results are

TABLE III.

Values and Signs of F(h0l).

					h.					
l.	0	2	4	6	8	10	12	14	16	18
11	—	−19	—	—	—	—	—	—	—	—
10	+ 13	−42·5	—	—	—	—	—	—	—	—
9	—	−14	—	—	—	—	—	—	—	—
8	− 28	+15	—	+16	—	—	—	—	—	—
7	+23·5	+24·5	+10	+56·5	—	−12	—	—	—	—
6	− 50	—	+35·5	+32	+26	—	—	—	—	—
5	− 59·5	−72	−13	+29	—	−17·5	—	—	—	—
4	+ 17	+ 9·5	−66·5	+26	+18·5	−19	−35	—	—	—
3	− 39	−13	—	−33	—	+13	—	—	—	—
2	−85	+ 5·5	—	−75·5	+21·5	−25	−11	+14	+15·5	—
1	+ 77·5	−92	−12·5	−37	—	—	—	−32·5	−10	—
0	+532	—	−45·5	+38	—	+11·5	+16	—	−15	—
$\bar{1}$	+ 77·5	+96·5	+80	−40	+20	+61·5	+12·5	—	−12·5	—
$\bar{2}$	− 85	+16·5	−85	−55	—	+20	—	—	+10	−26·5
$\bar{3}$	− 39	+67·5	−74	−30·5	+15	+28	−13	−29·5	—	—
$\bar{4}$	+ 17	−60·5	−48	—	—	+12·5	+52	− 9·5	−28·5	+25·5
$\bar{5}$	− 59·5	+36	−37·5	−16	−13	−13·5	+11·5	+11	—	+27
$\bar{6}$	− 50	—	—	+30·5	—	+27	−41	+16	—	—
$\bar{7}$	+23·5	+21·5	+42·5	+30·5	−14·5	—	−30·5	+ 9	—	—
$\bar{8}$	− 28	—	+58·5	+16·5	+41·5	−46	−42	−22	—	—
$\bar{9}$	—	—	+12·5	−22	+44	+14·5	−13	−36·5	+ 8·5	—
$\bar{10}$	+ 13	—	+16·5	—	−15	—	+10	—	+ 9·5	—
$\bar{11}$	—	−38	—	—	−38	—	—	—	+10	—
$\bar{12}$	—	—	−24	—	—	−12·5	+ 8·5	—	—	—
$\bar{13}$	—	+38	−16	−24·5	+27	+25	—	—	—	—
$\bar{14}$	—	—	—	−27	−18	—	+21	—	—	—

Fig. 2.



Projection along the b *axis, showing one complete phthalocyanine molecule. The plane of the molecule is steeply inclined to the plane of the projection, the* M *direction making an angle of* 46° *with the* b *axis, and the* L *direction* 2·3°. *Each contour line represents a density increment of one electron per* A.², *the one-electron line being dotted.*

represented by the contour map of Fig. 2, which is drawn by interpolation methods from the totals. It may be noted that the summations involve the addition of over 230,000 terms, but the numerical work can be considerably reduced by methods already described (*Phil. Mag.*, 1936, **21**, 176).

All the atoms in the molecule (except hydrogen) can be located without difficulty in the projection, and the positions of their centres can be determined with some accuracy. Hence, two co-ordinates (x and z) for each atom can be obtained directly, but the third co-ordinate (y), which is measured normal to the plane of the projection, is unknown. But the remarkable regularity of the structure makes it easy to estimate the y co-ordinates, and the results can later be checked against another projection of the structure described below.

It is convenient to refer the measurements to two principal molecular axes L and M (Fig. 2). When lines are drawn to connect opposite pairs of atoms, (11, 11′), (10, 12′), (9, 13′), (4, 18′), etc., it is found that these lines are all parallel to within ± 0·35°. The mean direction of 19 such lines is taken as the M axis, and this makes an angle of 22·9° with the a crystal axis (η_M). Similarly, lines connecting pairs of atoms above and below the centre (7, 7′), (8, 14), (9,13), etc., are also found to be parallel to within ± 0·4°, and their mean direction (L) makes an angle of 69·3° with the a axis (η_L).

The only simple explanation of this extreme regularity in an arbitary projection of the structure is that the whole molecule is planar. If the 38 lines mentioned above were not parallel in the actual molecule, it would be an extraordinary coincidence that they are parallel in this projection. This does not exclude the possibility of troughs running across the molecule, but the regularity of the distances (see below) and the presence of the centre of symmetry make this very unlikely.

The benzene rings at the four corners of the molecule are found to be the projections of regular plane hexagons, to within about 0·04 A.; *i.e.*, opposite sides are parallel to, and of one-half the length of, the line through the centre joining the other two corners. Now the size of the benzene ring has frequently been measured in organic compounds (*Proc. Roy. Soc.*, 1933, **142**, 659, etc.), and the most reliable value for the radius, or centre to centre distance, is 1·39 A. If we take this figure as a known dimension, the four benzene rings in the structure can then be used as "indicators," to determine the true orientation of the molecule in the crystal. For example, the benzene hexagons are greatly foreshortened in the M direction, indicating a considerable inclination of that axis of the molecule to the plane of the projection. Along the L axis the distances are practically those of normal rings, showing that the inclination of this axis to the plane of the projection must be small (less than 10°). Two of the four benzene rings are crystallographically independent, and the other two are inversions of these through the centre of symmetry. But as all four were drawn by independent interpolation from the summation totals, the results are given separately. The angle between the M axis and the b crystal axis is denoted by ψ_M and we have $\sin\psi_M = r/R$, where r is the measured length of a line in the projection, and R is the real length (inferred). In this way we obtain the following values for ψ_M from the four rings

Ring 1 . . . 4 $\psi_M = 46{\cdot}0^\circ$
,, 1′ . . . 4′ $\psi_M = 46{\cdot}3$
Ring 15 . . . 18 $\psi_M = 45{\cdot}0^\circ$
,, 15′ . . . 18′ $\psi_M = 46{\cdot}2$
Mean $\psi_M = 45{\cdot}9^\circ$.

The mean result for the inclination of the M axis of the molecule is probably accurate to within 1°. The inclination of the L axis, however, cannot be determined in this way, because when r/R is near unity the results are unreliable. But another method is available. The two molecular axes L and M are inclined at 92·2° to each other in the projection, ($\eta_L + \eta_M$), a figure which is probably accurate to within 0·2°, as it is the mean of 19 different pairs of lines. Now it is safe to assume that these two axes are at right angles in the actual molecule. If they were not, interatomic distances on one side of the molecule, including distances within the benzene ring, would be contracted, while corresponding distances on the other side would be relatively expanded, a condition which is extremely improbable. The apparent departure from perpendicularity of the axes L and M must be due to the orientation of the molecule and can therefore be used to give an accurate measure of the inclination of the L axis from the plane of the projection. We now have the necessary conditions for deriving the complete orientation of the molecule in the crystal. χ_L, ψ_L, and ω_L denote the real angles which the L axis makes with the a and b crystal axes and their perpendicular, while χ_M, ψ_M, and ω_M are the corresponding angles for the M axis. η_L and η_M are the observed angles which L and M make with the a axis in the projection. The conditions are

$$(1)\quad \cos^2\chi_L + \cos^2\psi_L + \cos^2\omega_L = 1$$
$$(2)\quad \cos^2\chi_M + \cos^2\psi_M + \cos^2\omega_M = 1$$
$$(3)\quad \cos\chi_L\cos\chi_M + \cos\psi_L\cos\psi_M + \cos\omega_L\cos\omega_M = 0$$
$$(4)\quad \cos\omega_L = \cos\chi_L\tan\eta_L$$
$$(5)\quad \cos\omega_M = \cos\chi_M\tan\eta_M$$
$$(6)\quad \psi_M = 45{\cdot}9^\circ$$

from which we obtain the following values for the direction cosines of the molecular axes

$$\begin{array}{llllll}
\chi_L = 69\cdot3^\circ, & \cos\chi_L = 0\cdot3532 & \chi_M = 48\cdot6^\circ, & \cos\chi_M = 0\cdot6615 & \chi_N = 131\cdot4^\circ, & \cos\chi_N = -0\cdot6617 \\
\psi_L = 87\cdot7^\circ, & \cos\psi_L = 0\cdot0395 & \psi_M = 45\cdot9^\circ, & \cos\psi_M = 0\cdot6960 & \psi_N = 44\cdot2^\circ, & \cos\psi_N = 0\cdot7169 \\
\omega_L = 20\cdot8^\circ, & \cos\omega_L = 0\cdot9347 & \omega_M = 106\cdot2^\circ, & \cos\omega_M = -0\cdot2794 & \omega_N = 77\cdot3^\circ, & \cos\omega_N = 0\cdot2197
\end{array}$$

The last three quantities refer to the direction of the normal to the molecular plane.

Molecular Dimensions and Co-ordinates.—Although all the carbon and nitrogen atoms in the molecule can be clearly seen in the projection of Fig. 2, the precision with which their centres can be determined necessarily varies in different parts of the projection, and can best be estimated by a study of the map. The nitrogen atoms 11 and 7 are most clearly defined, and in the benzene ring, atoms 2, 5, 16, and 19. The centres of these can be determined fairly accurately (± 0·02 A.), but the resolution of the other atoms is not quite so satisfactory. It is found, however, that projections of regular plane hexagons can be inscribed on the benzene rings, and that the atoms lie on the corners of these hexagons, with some possible small deviations in the case of the less perfectly resolved atoms, which are noted in the next section. The positions of the centres of all the atoms were estimated, and the co-ordinates measured parallel to the molecular axes L and M, with the results shown in Table IV.

TABLE IV.

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	5·05, 5·09	2·99, 3·04	±5·07	4·20
2, 16	4·05, 4·10	3·70, 3·72	±4·08	5·17
3, 17	2·72, 2·78	3·43, 3·42	±2·75	4·77
4, 18	2·39, 2·43	2·45, 2·46	±2·41	3·42
5, 19	3·39, 3·42	1·75, 1·77	$\pm3\cdot40_5$	2·45
6, 20	4·71, 4·75	2·02, 2·06	±4·73	2·84
7	3·43	0	±3·43	0
8, 14	2·70, 2·72	0·81, 0·81	±2·71	1·13
9, 13	1·39, 1·38	0·94, 0·96	±1·38	$1\cdot32_5$
10, 12	1·13, 1·15	1·90, 1·89	$\pm1\cdot14_5$	2·64
11	0	2·38	0	3·32

The atoms are grouped in symmetrical pairs above and below the M axis, and are denoted by the numbers in the first column. Individual measurements of the co-ordinates of these atoms are given by the next four numbers. The four-fold symmetry of the molecule is shown by the similarity of the co-ordinates of the two atoms in each pair. The differences are so small that they may be ascribed to experimental errors, and consequently the numbers have been averaged in the last two columns, and multiplied by the sines of the inclinations of the molecular axes to the projection axis (b), which reduces the measured values to actual molecular dimensions. From these figures the interatomic distances and valency angles are easily obtained, and the results are shown in Fig. 3. There is a possibility that atoms 8 and 14′ may lie about 0·04 A. nearer to 7 than is shown in Fig. 3. The positions assigned, however, make allowance for overlap, and seem the most probable.

The co-ordinates of the atoms referred to the crystal axes, which are required for calculating the structure factors, etc., are obtained by combining the molecular co-ordinates L and M with the orientation angles according to the relations

$$\begin{array}{ll}
x' = L\cos\chi_L + M\cos\chi_M & \\
y = L\cos\psi_L + M\cos\psi_M & x = x' - z'\cot\beta \\
z' = L\cos\omega_L + M\cos\omega_M & z = z'\operatorname{cosec}\beta
\end{array}$$

($x'yz'$) are rectangular co-ordinates referred to the a and b crystal axes and their perpendicular, and (xyz) are the monoclinic crystal co-ordinates. The numerical results are given in Table V. It should be noted that x and z can be obtained by direct measurement of the projection, but y can only be obtained by calculation.

DISCUSSION OF THE STRUCTURE.

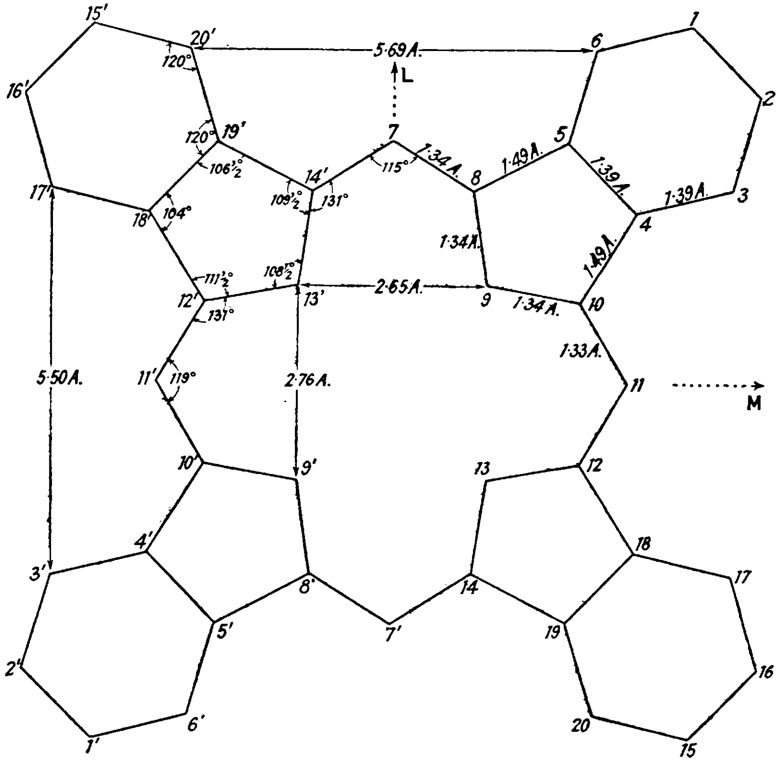
The molecular dimensions shown in Fig. 3 indicate the type of bond between the various atoms. The closed inner system consisting of 16 carbon and nitrogen atoms is one of great stability, and is of frequent occurrence in Nature, forming the nucleus of the porphyrins. The interatomic distance has the practically constant value of 1·34 A., with

TABLE V.

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

Atom (cf. Fig. 2).	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
1 CH	6·82	123·7°	3·12	238·1°	4·22	102·7°
2 CH	6·35	115·2	3·76	286·5	2·80	68·1
3 CH	4·91	89·0	3·43	261·5	1·46	35·6
4 C	3·94	71·3	2·48	189·0	1·53	37·3
5 C	4·40	79·8	1·84	140·6	2·95	71·8
6 CH	5·84	105·8	2·17	165·2	4·29	104·3
7 N	3·24	58·7	0·14	10·4	3·79	92·2
8 C	3·10	56·3	0·90	68·2	2·62	63·8
9 N	1·95	35·2	0·98	74·5	1·09	26·5
10 C	2·36	42·8	1·88	143·6	0·39	9·6
11 N	1·61	29·1	2·31	176·0	−1·10	− 26·7
12 C	0·20	3·7	1·79	136·7	−2·14	− 52·0
13 N	−0·66	− 12·0	0·87	66·1	−1·96	− 47·8
14 C	−2·01	− 36·4	0·68	52·0	−3·37	− 81·9
15 CH	−2·76	− 50·0	2·72	207·6	−6·99	−170·1
16 CH	−1·34	− 24·3	3·43	262·0	−6·21	−151·2
17 CH	−0·28	− 5·0	3·21	245·0	−4·61	−112·2
18 C	−0·61	− 11·1	2·29	174·5	−3·80	− 92·3
19 C	−2·02	− 36·6	1·57	119·9	−4·57	−111·2
20 CH	−3·08	− 55·8	1·79	136·6	−6·16	−150·0

FIG. 3.

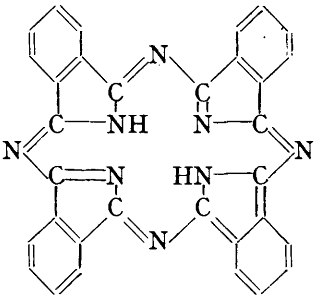


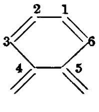
Dimensions of the phthalocyanine molecule.

an average possible error of about ± 0·03 A., a figure which points to single bond–double bond resonance between the carbon and nitrogen atoms.

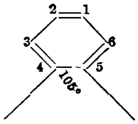
This inner system is connected to the benzene rings by carbon–carbon bonds of quite a different type, the distance here being 1·49 ± 0·03 A. If we use the empirical function expressing the dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance given by Pauling, Brockway, and Beach (*J. Amer. Chem. Soc.*, 1935, **57**, 2706), this distance of 1·49 A. would indicate from 12 to 15% of double-bond character in these links. This is very similar to the type of bond between conjugated benzene rings in diphenyl and *p*-diphenylbenzene (Dhar, *Indian J. Physics*, 1932, **7**, 43; Pickett, *Proc. Roy. Soc.*, 1933, *A*, **142**, 333). From the chemical structure (I), however, we should expect the somewhat higher double-bond character of 25%; but the main point of interest lies in the equality, within narrow limits, of these eight bonds which connect the benzene rings to the inner resonating system. This result emerges directly from the *X*-ray measurements.

(I.)





(II.)



(III.)

With regard to the benzene rings, the dimension of 1·39 A. was assumed in calculating the orientation of the molecules; but the fact that the rings appear as sensibly *regular* hexagons confirms the validity of this assumption. Some of the carbon atoms (*e.g.*, 1, 4, 6, 20) are not very perfectly resolved, and in order to see if any systematic deviations from regularity might exist, an attempt was made to estimate the centres of all the atoms independently, without trying to inscribe the projections of regular plane hexagons on the rings. The interatomic distances obtained were as follows (in A. units):

1, 2 = 1·39 4, 5 = 1·36 15, 16 = 1·35 18, 19 = 1·37
2, 3 = 1·40 5, 6 = 1·38 16, 17 = 1·39 19, 20 = 1·38
3, 4 = 1·44 6, 1 = 1·35 17, 18 = 1·38 20, 15 = 1·35

The angles were all within 3° of 120°. On the whole, systematic deviations do not seem to occur. The variations are, perhaps, not larger than might be expected from the lack of resolution of the atoms, due to incompleteness of the Fourier series and experimental errors.

There are two conflicting possibilities, either of which might affect the dimensions of the benzene rings in this structure. If the links connecting them to the inner system have sufficiently high double-bond character, there might be a tendency to *o*-quinonoid ring formation, as in (II). On the other hand, measurement of the angles in the *iso*indole ring (compare Fig. 3) shows that the links emerging from the benzene rings are very considerably strained out of the normal (120°) positions, the mean value of the two angles being about 105°. Following the work of Mills and Nixon (J., 1930, 2510), and more recently of Sidgwick and Springall (this vol., in the press), this might lead us to expect a different stabilisation of the Kekulé forms, as shown in (III). In both (II) and (III) the 4, 5 link might be expected to exhibit a certain degree of single-bond character beyond the other links, but there is no experimental evidence of this in our results.

There does exist, however, another distortion, affecting the whole molecule, which appears to be large enough to permit of fairly definite measurement. This is a departure from true tetragonal symmetry, and is best seen by comparing the lengths of the horizontal and vertical lines joining corresponding pairs of atoms (compare Fig. 3 and Table IV). Taking first the lines connecting atoms on the inner carbon–nitrogen system, the lengths (in A.) are

Horizontal lines. Vertical lines.
8, 14′ = 2·26 10, 12′ = 5·28 10, 12 = 2·29 8, 14 = 5·42
9, 13′ = 2·65 11, 11′ = 6·64 9, 13 = 2·76 7, 7′ = 6·86

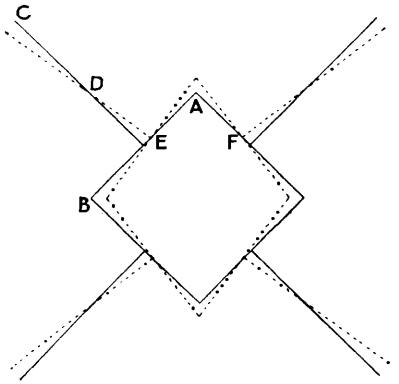
The horizontal lines are all shorter than the corresponding vertical lines, the discrepancy increasing as we descend from the apex of the molecule at the nitrogen atom 7. If, however, the lines are taken to connect corresponding atoms on the benzene rings, the situation is reversed, the *horizontal* dimensions in Fig. 3 being the greater, as shown below.

Horizontal lines.		Vertical lines.	
1, 15′ = 8·40	5, 19′ = 4·90	2, 16 = 8·16	4, 18 = 4·82
6, 20′ = 5·69	3, 17′ = 9·54	3, 17 = 5·50	6, 20 = 9·46
2, 16′ = 10·34	4, 18′ = 6·84	1, 15 = 10·14	5, 19 = 6·81

In this case the discrepancy diminishes as we descend from the highest line, 1, 15′.

It is impossible to explain these two contrary departures from true tetragonal symmetry by an error in calculating the orientation of the molecule, and the differences seem much too systematic to be accounted for by random experimental errors, or deficiencies in the Fourier series. They can be explained very easily by the simplified model shown in Fig. 4, where the zig-zag C–N links (7, 8, 9, 10, 11) are replaced by the straight line AB. The benzene ring is situated on the outer portion of the line CD. If a distortion is caused, *e.g.*, by a force operating between E and F, the dotted lines show that the dimensions change in a manner which explains all the measurements given above, at least qualitatively. The angle at A will diminish, and that at B will increase. In the actual molecule these angles are 115° and 119°.

Fig. 4.



Simplified model of the phthalocyanine molecule.

EF in the simple model corresponds to the distance between the *iso*indole nitrogen atoms (9, 13′) in the molecule, which is 2·65 A. Now this distance is just about the right order for hydrogen-bond formation as between oxygen atoms in acids and acid salts (Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367, etc.). Quantitative data on the distances involved in hydrogen-bond formation between nitrogen atoms are not available, but there seems little doubt that they can occur. The presence of such *internal* hydrogen bonds in the phthalocyanine molecule would help to explain the distortion from true tetragonal symmetry.

Another Projection of the Structure.—No other projection of the structure is possible which gives a resolution of the atoms in any way approaching that obtained along the b axis. If we try to make a projection nearly normal to the plane of the molecule, other interleaving molecules come behind, and the resulting diagram is hopelessly obscured. It is, however, important to study the other zones of reflections to obtain more direct confirmation of the values assigned to the y co-ordinates, which are based upon the calculated orientation and assumed flatness of the molecule. When the structure factors for these other zones are calculated from the co-ordinates in Table V, good agreements with the observed values are obtained, of which details will be given in a later paper. The projection along the c axis, corresponding to the $(hk0)$ zone of reflections, has been chosen for detailed study, and a Fourier synthesis is given in Fig. 5. The coefficients are given in Table VI. The signs, or phase constants, of the $(h + k)$ even planes were obtained in the same direct manner as before, but for the $(h + k)$ odd planes the signs are from the calculated values of the structure factors.

The drawing to the right of the contour map is prepared from the co-ordinates in Table V (atoms half size) and shows the complicated way in which seven phthalocyanine molecules overlap in this projection. Only the portion within the dotted line, representing one unit cell, is complete.

Only the atoms 3 and 3′ are separately resolved in this projection of the structure, but a careful study of the map shows that the contour lines correspond faithfully to the calculated

TABLE VI.

Values and Signs of F(hk0).

			k.		
h.	0	1	2	3	4
16	− 15	—	—	—	—
15	—	—	—	—	—
14	—	—	+17·5	—	—
13	—	—	—	—	—
12	+ 16	—	−12	—	—
11	—	—	+36	—	—
10	+11·5	+16	—	−22·5	—
9	—	−28	—	—	—
8	—	−12·5	−10	—	—
7	—	—	—	—	−16
6	+ 38	+10	+14·5	—	—
5	—	—	+31·5	+13	—
4	− 45·5	+20·5	—	—	—
3	—	−19	—	—	—
2	—	−52·5	−10·5	—	—
1	—	−65·5	—	−14·5	+10·5
0	+532	—	−10	—	+ 6

			k.		
h.	0	1	2	3	4
$\bar{1}$	—	−65·5	—	−14·5	−10·5
$\bar{2}$	—	+52·5	−10·5	—	—
$\bar{3}$	—	−19	—	—	—
$\bar{4}$	−45·5	−20·5	—	—	—
$\bar{5}$	—	—	−31·5	+13	—
$\bar{6}$	+38	−10	+14·5	—	—
$\bar{7}$	—	—	—	—	+16
$\bar{8}$	—	+12·5	−10	—	—
$\bar{9}$	—	−28	—	—	—
$\bar{1}\bar{0}$	+11·5	−16	—	+22·5	—
$\bar{1}\bar{1}$	—	—	−36	—	—
$\bar{1}\bar{2}$	+16	—	−12	—	—
$\bar{1}\bar{3}$	—	—	—	—	—
$\bar{1}\bar{4}$	—	—	+17·5	—	—
$\bar{1}\bar{5}$	—	—	—	—	—
$\bar{1}\bar{6}$	−15	—	—	—	—

positions of the atoms. This is especially evident near the empty portions of the structure at the centre, and at the centres of the benzene rings. If any considerable distortion from the planar form existed in the molecule, it would be evident from this projection.

The co-ordinates of atom 3 estimated from this projection compare with the previous values as follows :

	x, A.	*y*, A.
Measured from *c* projection	4·78	3·34
From *b* projection and calc. orientation	4·91	3·43

The agreements are perhaps as close as can be expected, in view of the unsatisfactory nature of this projection, and the difficulty of making accurate intensity measurements in this zone.

Intermolecular Distances and Arrangement of Molecules in the Crystal.

The way in which the phthalocyanine molecules interlock to form the crystal is shown by the group in Fig. 6, which is a small-scale reproduction of the *b*-axis projection. Although appearing identical in this projection, the planes of the molecules are actually inclined in opposite directions to the plane of the projection (010). Thus, if the two end molecules in the lower row are inclined to the right, the middle one is inclined to the left, and the two end ones of the upper row are inclined to the left. The molecular planes are inclined at 44·2° to the (010) plane, and consequently the planes of adjacent molecules are almost perpendicular.

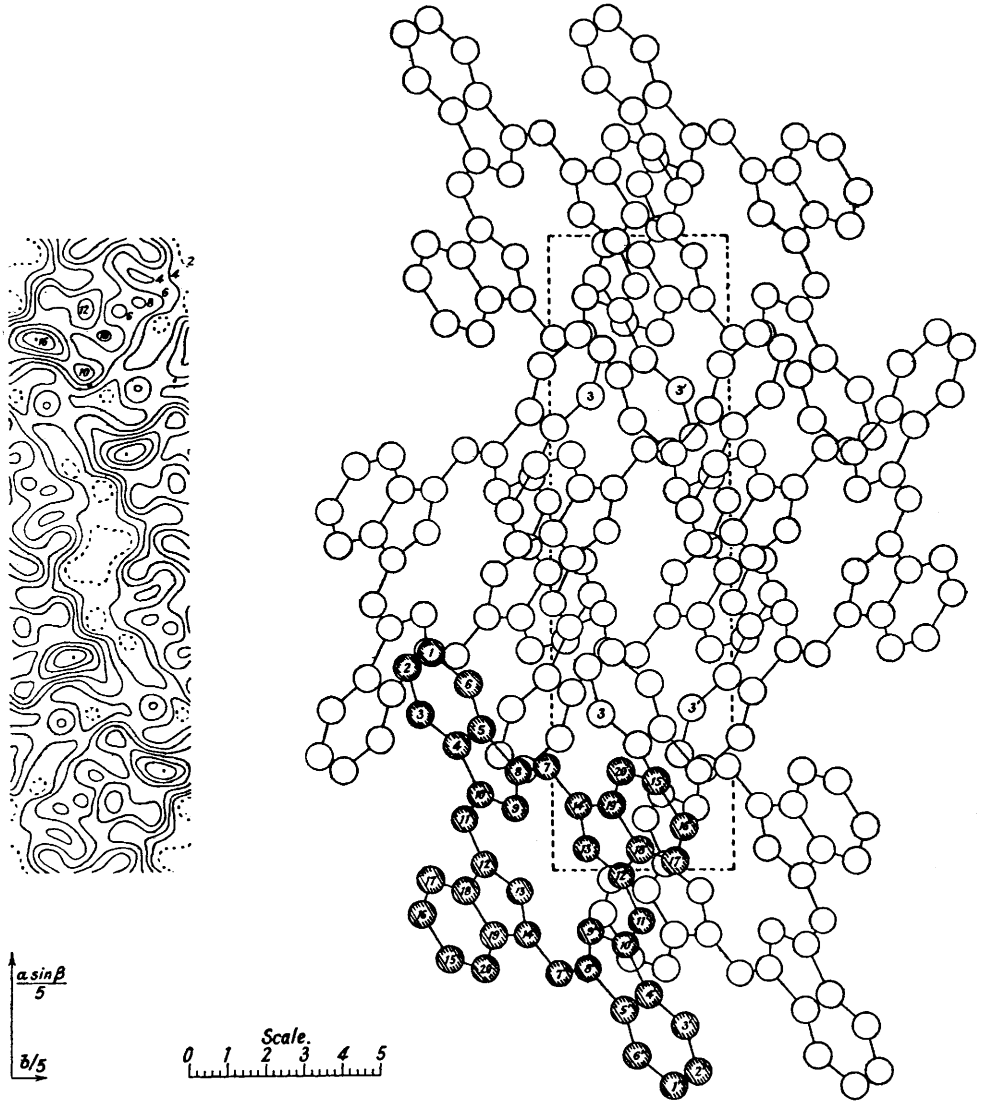
Identical molecules recur along the *b* axis at intervals of 4·72 A., and the perpendicular distance between the planes of these parallel molecules is $b.\cos\psi_N = 3{\cdot}38$ A., almost identical with the interlaminar distance in graphite (3·41 A.). When a projection is taken normal to the molecular planes, none of the atoms in the parallel molecules at either end of the *b* axis comes exactly over another, the nearest approaches being between 17 and 14, and between 3 and 8 (carbon atoms) where the distances are *3·41* A. The nitrogen atoms 13 and 9 are nearly as close, the distance being *3·44* A.

The shortest intermolecular distance which has been found in the whole structure occurs between the benzene carbon atom 2 on the standard molecule, and the nitrogen atom 11′ on the reflected molecule ($\frac{1}{2}a$, $\frac{1}{2}b$, removed) where the value is *3·35* A. No other approach of less than 3·5 A. has been found, although between the benzene carbon 1 on the standard molecule and the benzene carbon 15 on the reflected molecule one translation along the *c* axis and one translation along the *b* axis, the distance is as low as *3·63* A. These results show that the usual order of minimum intermolecular distance, which occurs when only van der Waals forces are operative between the molecules, is maintained in the phthalocyanine structure.

SUMMARY.

The structure of phthalocyanine has been determined by direct *X*-ray analysis of the crystal. The usual difficulty of the unknown phase constant, which necessitates a preliminary analysis by trial, has been overcome by comparing absolute measurements of corresponding reflections from nickel phthalocyanine and the metal-free compound, which leads to a direct determination of all the significant phase constants in the ($h0l$) zones of the two compounds, numbering about 300. A Fourier analysis of these results determines two co-ordinates of each carbon and nitrogen atom in the structure, and the regularity of the projection shows beyond doubt that the molecule is planar. The orientation

FIG. 5.

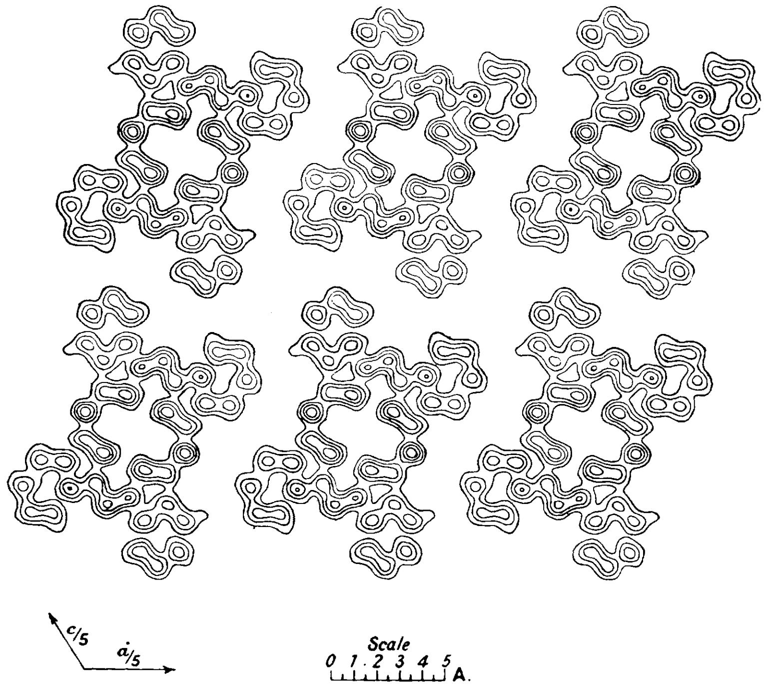


Projection along the c *axis showing the complete unit cell, and how parts of seven phthalocyanine molecules contribute to the structure. Each contour line represents* 2 *electrons per* A.², *the two-electron line being dotted.*

of the molecule in the crystal is deduced, and the third co-ordinates of the atoms calculated. The results are then confirmed by a second Fourier projection of the structure, along the *c* axis.

The results show that the chemical structure assigned to the compound by Linstead is correct, and give further information about the type of valency bonds. The inner nucleus of the molecule, which is common to the porphyrins, consists of a closed system of 16 carbon and nitrogen atoms, which appear to be in a state of double bond–single bond resonance, the interatomic distance having the appreciably constant value of 1·34 ± 0·03 A. This inner system is connected to the four benzene rings by C–C bonds of length 1·49 ± 0·03 A., which indicates a small percentage of double-bond character. The benzene rings are sensibly regular, such variations in their C–C distance as do occur being of small order and apparently erratic, probably owing to deficiencies in the Fourier series. The carbon links emerging from the benzene rings are strained about 15° from their normal positions. In addition, the molecule as a whole suffers a small distortion from true tetragonal symmetry, probably due to the existence of an internal hydrogen bond between the two *iso*indole nitrogen atoms.

FIG. 6.



A group of phthalocyanine molecules in the b *axis projection. Each contour line represents two electrons per* A.^{2}.

In the crystal, the planes of adjoining rows of molecules are almost at right angles, and the minimum intermolecular approach distance is 3·35 A. The perpendicular distance between the molecular planes of parallel molecules is 3·38 A.

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ROYAL INSTITUTION.

[*Received, June* 26*th*, 1936.]