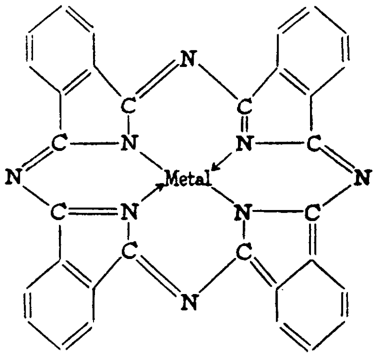
110. X-*Ray Studies of the Porphins.*

By Ida Woodward.

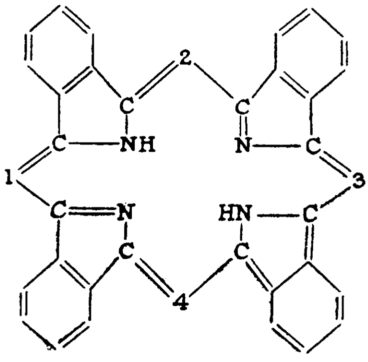
A preliminary *X*-ray examination of tetrabenzporphin and tetrabenzmonazaporphin shows that, although belonging to the same space group $C_{2h}^5(P2_1/a)$ as the phthalocyanines, they differ considerably from the latter in the cell dimensions. The *b*-axis has increased from 4·7 A. to 6·6 A., the *a* and *c* axes being diminished so that the volume of the unit cell is little altered, and the β angle is practically unchanged. Considerable alterations in the intensities of the reflexions are also observed. These changes cannot be accounted for without assuming a considerable change in the packing of the molecules.

Information of interest, for theories both of molecular structure and of the packing of molecules, can be obtained from an *X*-ray study of the phthalocyanines and related compounds. Small chemical changes, such as the substitution of a metal for hydrogen, or of one or more –CH= groups for –N=, must slightly modify the resonance forces in the molecule and in consequence affect its detailed structure and also its packing in the crystal.

A preliminary account is now given of the effect of the replacement of three and four nitrogen atoms by CH groups. In the following scheme and table are shown the compounds so far investigated, the data in the last two columns being new.



Phthalocyanine, various metal derivatives.



Metal-free phthalocyanine	*Nitrogen at* 1, 2, 3 *and* 4.
Tetrabenztriazaporphin	CH *group at* 1. *Nitrogen at* 2, 3 *and* 4.
Tetrabenzmonazaporphin	CH *group at* 1, 2 *and* 3. *Nitrogen at* 4.
Tetrabenzporphin	CH *group at* 1, 2, 3 *and* 4.

Crystal Data of Phthalocyanines and Porphins.

	Platinum phthalocyanine,[1] $C_{32}H_{16}N_8Pt$.	Nickel phthalocyanine,[2] $C_{32}H_{16}N_8Ni$.	Phthalocyanine,[3] $C_{32}H_{18}N_8$.	Tetrabenztriazaporphin,[4] $C_{33}H_{19}N_7$.	Tetrabenzmonazaporphin, $C_{35}H_{21}N_5$.	Tetrabenzporphin, $C_{36}H_{22}N_4$.
a, A.	23·9	19·9	19·85	19·85	17·6	17·2
b, A.	3·81	4·71	4·72	4·72	6·61	6·61
c, A.	16·9	14·9	14·8	14·8	12·5	12·2
β	129·6°	121·9°	122·25°	122·25°	122·7°	122·5°
Volume of unit cell, A.^{3}	1186	1186	1173	1173	1218	1165
d (flotation)	1·98	1·63	1·44	—	1·40	1·38
d (calc.)	1·97	1·59	1·445	—	1·39	1·46
No. of electrons per unit cell	684	584	532	532	532	532

[1] Robertson and Woodward, this vol., p. 36
[2] *Idem*, J., 1937, 219
[3] Robertson, J., 1936, 1195
} detailed studies.
[4] *Idem*, J., 1939, 1811.

In all cases there are two molecules per unit cell, and the space group is $C_{2h}^5(P2_1/a)$. The probable errors in the new data are estimated to be: for tetrabenzmonazaporphin,

± 1% for *b* and *c* and ± 2% for *a*, ± 1° for the angle β and ± 0·02 for *d* (flotation); for tetrabenzporphin, ± 4% for *a* and *c*, ± 1% for *b*, ± 2° for the angle β, and ± 2% for *d* (flotation).

Discussion of Structure.—The table shows a striking change in the axial lengths as we pass from tetrabenztriaza- to tetrabenzmonaza-porphin. A similar but less marked difference exists between those of platinum phthalocyanine and nickel or metal-free phthalocyanine. In the last two, the detailed study of the structure has shown that the approximately square, flat molecules are of nearly the same size, which therefore depends little on the central hydrogen atoms. The change in cell dimensions is due to a difference in molecular packing on introducing platinum. In both methods of packing, one edge of the square molecule is almost parallel to the (010) plane, being inclined to it at about 2°, and the other edge is inclined at an angle of about 27° for platinum and about 44° for nickel and metal-free phthalocyanine. The perpendicular distance between the successive molecules lying along the *b*-axis remains practically unchanged, being about 3·38 A.

If we assume for the molecules of tetrabenzmonazaporphin the same general size and shape and the same distance, 3·38 A., between the parallel molecules situated along the *b*-axis, the angle between the plane of the molecule and the (010) plane must be about 60°. The further assumption being made that one edge of the square is again near the (010) plane, it does not seem possible to account for the observed intensities of the main reflexions in the (*h*0*l*) zone. It is necessary, therefore, to suppose that some further change in the orientation takes place, as, *e.g.*, that both sides of the square are considerably inclined to the (010) plane. An alternative supposition is that the more complete substitution of –CH= groups for –N= may cause an appreciable change in the shape of the molecule. An investigation on the lines adopted for metal-free phthalocyanine and its nickel derivative would appear to be required to give a detailed solution.

EXPERIMENTAL.

Tetrabenzporphin.—No crystal of tetrabenzporphin really satisfactory for *X*-ray examination could be found among the small supply of material available, and although the *b*-axis was determined in the usual way by measurements of a fixed-plate rotation photograph about that axis, the *a* and *c* axes and the angle β were found from a rather poor *b*-axis rotation photograph taken on the two-crystal moving-film spectrometer (Robertson, *Phil. Mag.*, 1934, **18**, 729). No significant difference could be detected, in either the spacing or the intensity of the reflexions, between these and the corresponding photographs of tetrabenzmonazaporphin. From this it follows that there is little difference between the two compounds as regards the dimensions and arrangement of the molecules, and that tetrabenzporphin belongs to the same space group, $C_{2h}^{5}(P2_1/a)$ as tetrabenzmonazaporphin.

Tetrabenzmonazaporphin.—For tetrabenzmonazaporphin more reliable results could be obtained. Fixed-plate and moving-film rotation photographs were taken about all three axes. A further rotation photograph about the [102] axis gave its measured length as 21·25 A., whereas the value calculated from *a*, *c*, and β given above is 21·38 A. The angle β was obtained by goniometer readings of the angles between the reflexions from the faces of the crystal.

The crystals, like those of the phthalocyanines, are opaque, dark blue in colour with a metallic sheen, and elongate along the *b*-axis to form friable laths. No end faces were observed, the laths being terminated by fracture, or tapering gradually. The flat face of the lath was found to be the (20$\bar{1}$) plane, and the (001) was also developed, though much less strongly. The (100) was also found in some cases, but was in general very feebly developed. It is noteworthy that in the phthalocyanines the flat face of the lath is the (001).

Many aggregates of very slender crystals, with their *b*-axes almost parallel, were observed, and it was, in fact, difficult to find specimens consisting of only one crystal. These aggregates split up readily, but the component parts were in general too small to be of use.

A visual estimate of the intensities of the reflexions on the moving-film rotation photographs of tetrabenzmonazaporphin showed that they differ in a very marked degree from those given by metal-free phthalocyanine. For instance, the (200) reflexion is comparable in intensity with the (001), and the (20$\bar{2}$), comparatively weak in phthalocyanine, is for tetrabenzmonazaporphin second in intensity only to the (400) reflexion.

It should be noted that the molecular symmetry (centre) required by the space group

$C_{2h}^5(P2_1/a)$ is at variance with the chemical requirements. This may be due, as has already been pointed out in the analogous case of tetrabenztriazaporphin (Robertson, J., **1939**, **1811**), to the existence of an undetected super-lattice, or to a statistical distribution of the molecules with regard to the unique nitrogen atom. Calculation shows that the intensities of the reflexions from such a super-lattice, if it existed, would be far too faint to be detected in the present investigation.

Magnetic Data.—Some information concerning the magnetic properties of tetrabenzmonazaporphin has been kindly provided by Mrs. Lonsdale. Although the small amount of material available and the small size of the individual crystals prevented detailed magnetic measurements, it could be established that the crystals are strongly anisotropic, the maximum magnetic susceptibility being normal to the $(20\bar{1})$ plane. The minimum susceptibility, perpendicular to the *b* axis in the $(20\bar{1})$ plane, was found to be very nearly equal in magnitude to that (-166×10^{-6}) of phthalocyanine, but in the latter case it was perpendicular to the (001) (Lonsdale, J., **1938**, **365**).

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