The Location of the Inner Hydrogen Atoms of Phthalocyanine: a Neutron Diffraction Study

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THERE has been much speculation about the positions of the inner hydrogen atoms of the phthalocyanine molecule and the manner in which they are bonded. A variety of physicochemical investigations bearing on this question has been reported and several conflicting interpretations have been drawn from them; these have been reviewed elsewhere.[1]

We report here a neutron diffraction study of phthalocyanine which shows conclusively that the two inner hydrogen atoms lie in the plane of the so-called "great ring". These two hydrogen atoms are disordered so that on the average one half a hydrogen atom is associated with each pyrrole nitrogen atom, in a fashion similar to that observed for two of the porphine structures.[2]

Crystal data: $C_{32}H_{18}N_8$, $M = 514$, monoclinic, $a = 19{\cdot}86$, $b = 4{\cdot}73_4$, $c = 14{\cdot}80$ Å, $\beta = 122{\cdot}0°$, $U = 1180$ Å^3, $Z = 2$, space group $P2_1/a$ (C^5_{2h}; No. 14). Neutron wavelength was 1·237 Å. The crystal used for the study was grown by vacuum sublimation and was of good quality; its approximate dimensions were 5·0 × 1·0 × 1·0 mm. A manually set neutron diffractometer was used from which 964 intensity measurements were obtained.

The starting point for the crystallographic calculations was the set of co-ordinates for the carbon and nitrogen atoms, reported by Robertson,[3] together with co-ordinates for the outer hydrogen atoms (*i.e.* those attached to the benzene rings) which were estimated on the assumption that normal bonding arrangements prevailed. Preliminary scale and temperature factors were based on this model and were used to calculate a set of structure factors. The remaining two hydrogen atoms of the molecule, that is the inner hydrogen atoms, were clearly evident in the resulting three-dimensional difference map where they appeared as four well defined half-hydrogen atoms, one associated with each of the pyrrole nitrogen atoms.

The structure parameters were refined by the full-matrix least-squares method initially incorporating individual isotropic temperature factors and then anisotropic thermal parameters; occupancy factors for the half-hydrogen atoms were also included as parameters in the refinement. At the present stage of refinement R is 0·070; with isotropic temperature factors only, the refinement converged at R = 0·098.

The bond distances and angles are shown in the Figure. The current values of the estimated standard deviations are: for bond distances which do not involve hydrogen atoms, approximately 0·02 Å; for C–H distances, approximately 0·04 Å; and for the nitrogen to half-hydrogen atom distances, approximately 0·05 Å. It can be seen that the lengths of those bonds which are expected to be chemically equivalent do not differ significantly from each other and that all dimensions given here compare favourably with those found for previously reported comparable molecules.[2-5]

All atoms of the molecule, including the half-hydrogen atoms are coplanar within limits which are of the order of the probable errors calculated from the estimated standard deviations. The mean deviations from the plane are, for the half-hydrogen atoms, 0·05 Å, and for the other atoms, 0·04 Å.

The inner half-hydrogen atoms lie very nearly on the lines which join the centrosymmetrically related pyrrole nitrogen atoms. The average nitrogen to half-hydrogen atom distance of 0·94 Å is close to the normal covalent bond distances previously observed between hydrogen and nitrogen atoms.[5]

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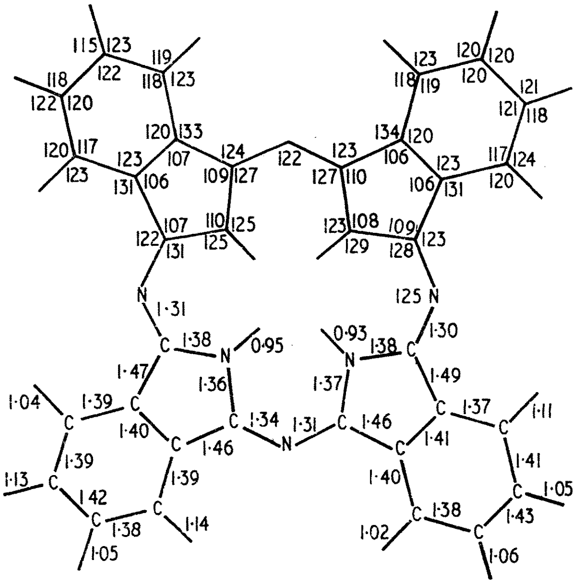

FIGURE. *Atomic disposition and molecular dimensions of the phthalocyanine molecule.*

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