X-Ray Crystal Structure of Octaethylporphinium (Monocation) Tri-iodide

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Summary X-Ray analysis shows that in the porphyrin monocation one pyrrole ring, probably protonated, is tilted 14° from the plane through the other three pyrrole rings by the repulsions between the inner three hydrogen atoms.

PORHHYRINS can exist in acidic solution as the free base, or as monocationic and dicationic species.[1] X-Ray analyses have shown that the free base[2] is planar within $\pm 0{\cdot}05$ Å, whilst the dication[3] is deformed considerably by the repulsions between the four inner hydrogen atoms and assumes $\bar{4}$ symmetry. The structure of the monocation is still unknown, but a different deformation was expected since it shows spectroscopic features different from those of the former two forms.[4] The present investigation is the first report of the structure of a porphyrin monocation.

Octaethylporphinium (monocation) tri-iodide, isolated from a methanolic solution of its dication iodide,[4] was recrystallized from $CHCl_3$–C_6H_6. Crystal data: $C_{36}H_{47}I_3N_4$, space group *Cmca*, $a = 29{\cdot}52(2)$, $b = 14{\cdot}49(7)$, $c = 17{\cdot}415(9)$ Å, $D_m = 1{\cdot}61$, $D_c = 1{\cdot}59$ g cm^{-3}, $Z = 8$.

Three-dimensional intensity data were collected on Weissenberg (Cu-K_α) and precession (Mo-K_α) photographs and measured by a TV densitometer.[5] Of 1938 possible reflexions, 1002 were non-zero. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The final R factor is 0·109.

The structure of the monocation (Figure) has a crystallographic mirror plane passing through N(1) and N(3), and lying perpendicular to the macrocyclic plane. The C–N–C angle in ring A, 102°, is significantly smaller than those in the rings B, B* (mirror image of B) and C, namely, 109 and 110°. This difference indicates that ring A is of pyrrolenine type, and the other three being of pyrrole type. The difference in the C–N distances for ring A and for the others is also consistent with this assignment. The inner three hydrogen atoms are, therefore, considered to be bonded to rings B, B*, and C.

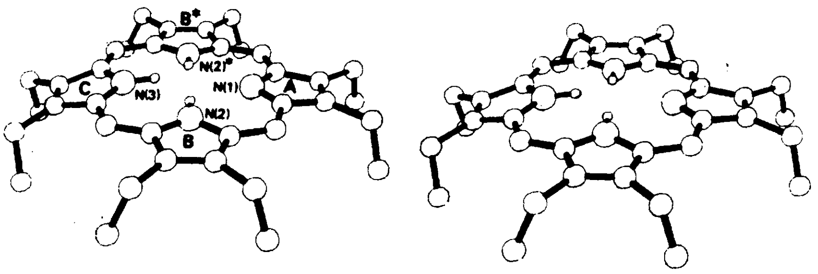

FIGURE. Stereoscopic view of the structure of octaethylporphin monocation.

The bond distances and angles in the other part of the monocation agree with those found in the free bases.[2] No hydrogen bonds are found between the pyrrole-type nitrogen atom and either the tri-iodide anion or the pyrrolenine-type nitrogen atom of a neighbouring monocation. The monocation comes into contact with the anion only through the peripheral ethyl groups, thus confirming the previous suggestion[4] based on i.r. spectra.

Rings A, B, and B*, are coplanar within ±0·03 Å, and their mean plane is inclined 14° to that of ring C. This inclination of ring C may arise from the repulsions between the inner three hydrogen atoms. The distance between H(B) and H(C), would be 1·54 Å, if the N–H distance is taken as 1·0 Å and the nitrogen atoms are assumed to be sp^2 hybridized. Even if N(3) were sp^3, H···H would be 2·14 Å, which is considerably shorter than twice the van der Waals radius (1·2 Å) of hydrogen. Therefore all three pyrrole-type nitrogen atoms may have to assume sp^3 character to some extent. In the i.r. spectrum, two sharp absorptions are observed around 3330 cm^{-1}, which could be assigned to stretching vibrations of the two crystallographically independent N–H bonds.

The abovementioned structure implies that the positive charge would be mostly localized at N(3) and that the three inner hydrogen atoms might impede insertion of metal ion into the monocation. Indeed, in recent kinetic studies on the formation of metalloporphyrins,[6] the cationic species of porphyrins were regarded as unreactive.

As the equilibrium between the free base and the monocation is sensitive to pH and other factors,[6] the cationic species could exist in a biological environment.[7] It might then be supposed that in the final stage of oxidation from porphyrinogen to porphyrin, which occurs in the mitochondria[8] or in cytoplasm,[9] the monocationic species plays a role in controlling the formation of metalloporphrins.

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