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MOLECULAR STRUCTURE AND FLUORESCENCE BEHAVIOUR OF A BENZOQUINONE/PORPHYRIN/BENZOQUINONE SANDWICH-MOLECULE

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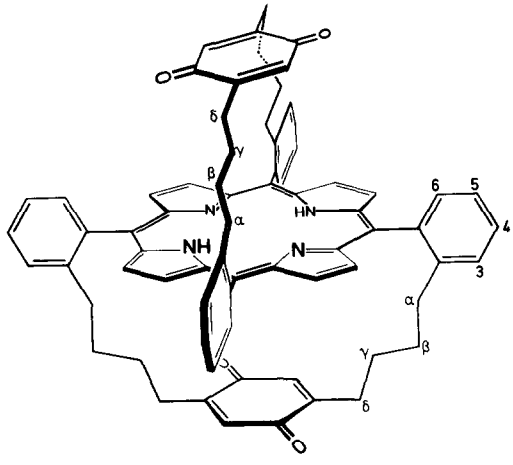
Summary: For the benzoquinone/porphyrin/benzoquinone sandwich-molecule 1 a highly symmetrical structure with parallel ring planes and interplanar distances of 342 pm was derived from X-ray analysis. 1 shows, in comparison to 2, a very strong quenching of fluorescence indicating intramolecular electron transfer.

Recently, we described the synthesis and characterisation of the benzoquinone/porphyrin/benzoquinone sandwich-molecule 1 [1]. We now report on the X-ray analysis of the molecular structure of 1 and on fluorescence measurements of 1 in comparison to the non-quinoid analogue 2.



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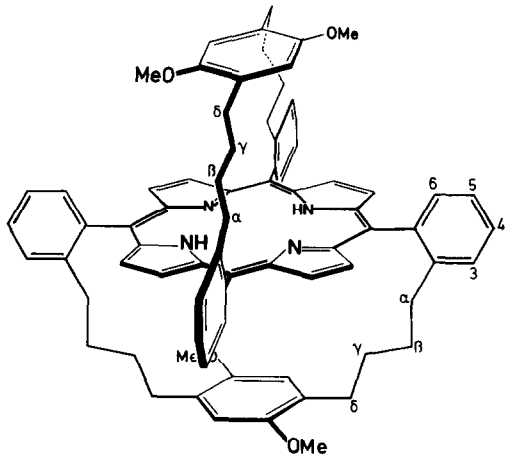

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X-Ray Structure Analysis of 1: 1 (violet crystals, m. p. 281 - 282°C) forms tetragonal prisms of the space group $I\bar{4}$ with the cell dimensions a = 1757.1(2), c = 1021.3(1) pm, and Z = 2. Intensity data were collected by using graphite-monochromated Mo-K_α radiation [2011 measured symmetry-independent reflections, 1209 reflections with $I \geq 1.96\,\sigma(I)$].

The structure could not be solved by direct methods. The molecule was positioned in the elementary cell according to its S_4 symmetry with the porphyrin ring [atoms N,C(1)....C(5)] within the (001) plane (cf. Figure 1A for the numbering of atoms). This position was opti=

mized by rotation of the molecule around the symmetry-axis (c-axis), and the coordinates of the remaining non-hydrogen atoms [C(6)....C(18), O(17')] were obtained by repeated Fourier syntheses taking into account a disorder for C(14) (two positions about 100 pm apart, g = 0.6 and 0.4). Full-matrix least-squares refinement using anisotropic temperature factors for non-hydrogen atoms led to a convergence at R = 0.12. By further difference Fourier synthesis significant remaining maxima were interpreted satisfactorily by assuming an inclusion of the solvent dichloromethane. Taking this into account with anisotropic temperature factors and using isotropic temperature factors for hydrogen atoms [with the exception of the hydrogens in the disorder area C(13) - C(14) - C(15)] the refinement converged at R = 0.057.

Molecular Structure of 1: According to the S_4-symmetry the two quinone rings are exactly parallel to each other and to the least-squares plane of the porphyrin system. As is seen from the top-view of the molecule (Figure 1A) the axes through the bridgehead atoms of the two quinone rings are perpendicular to each other, and the centers of all three ring systems of the sandwich-molecule are exactly superposed. The transanular distance between the porphyrin and the benzoquinones on both sides is 342 pm. As figure 1B indicates the porphyrin ring shows considerable deviation from planarity which results mainly from an inclination of 9^0 of the pyrrole rings against the least-squares plane of the porphyrin. The pyrrole rings themselves are nearly planar the maximum deviation from the plane through the five ring atoms being in the order of 1 pm. The phenyl substituents in the meso-positions C(5) of the porphyrin ring are twisted against the porphyrin plane by 67^0. Bond lengths and bond angles of 1 do not show any striking differences from normal values. - The X-ray analysis of 1 confirms in detail the highly symmetrical molecular structure with a parallel and centered arrangement of the three rings as predicted from molecular models and as indicated by ^{1}H NMR data [1].

Crystal Packing of 1: The molecules of 1 form stacks with the stacking axis perpendicular to the ring planes along the fourfold rotary inversion axis (c-axis). According to this symmetry, neighbouring molecules within these stacks are oriented in such a way that the axes of the two quinone rings opposing each other are crossed at 90^0. The intermolecular distance between these quinone rings is slightly shorter (337 pm) than the intramolecular distance between quinone and porphyrin planes. The included solvent molecules (see above) are accommodated in channels parallel to the 1 - stacks along the c-axis.

Fluorescence Measurements on 1 and 2: Photo-induced electron-transfer reactions from porphyrins to benzoquinones are of considerable biochemical interest. Synthesis and structure analysis of 1, as of other porphyrin/benzoquinone systems [1], were started in order to understand better the requirements of this electron-transfer reaction with regard to the mutual sterical arrangement of the two interacting moieties. First indications of an electron-transfer from porphyrin to benzoquinone were derived by comparing the fluorescence behaviour of 1 with the analogous doubly-bridged porphyrin 2 which is missing the quinoid structure: For 2 [$1 \cdot 10^{-6}$ molar solution in benzene (degassed with argon)] on excitation at 420 nm a strong fluorescence with maxima at 722 and 652 nm is observed. As is shown by comparison with tetraphenylporphyrin (TPP), measured under the same conditions, the fluorescence of 2 is the typical vibration-structured $S_1 \rightarrow S_0$ emission of the porphyrin chromophore which obviously is

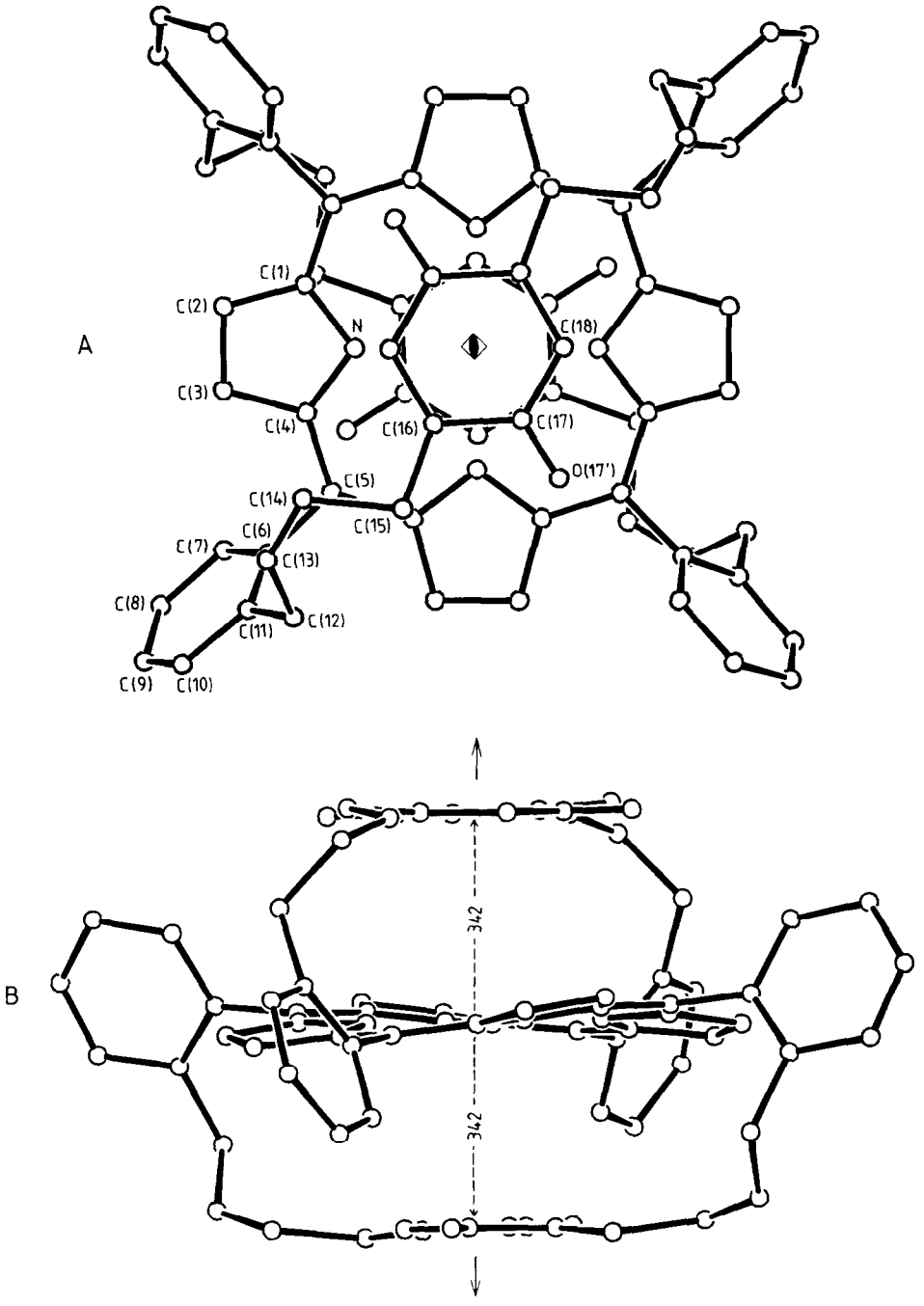

Figure 1. Molecular Structure of 1 in a Top-View Perpendicular to the Ring Planes (A) and in a Side-View (B).

nearly unaffected by transanular π...π-interaction of the porphyrin with the aromatic systems (Figure 2). In relation to the fluorescence quantum yield of TPP (ϕ = 0.13) [2] the quantum yield of the fluorescence of 2 can be estimated to approximately ϕ = 0.07. For 1, on the

other hand, the porphyrin fluorescence, again measured under the conditions mentioned for 2, is almost completely quenched the quantum yield being at least by a factor of 100 smaller than for 2 (whether the remaining fluorescence is at all real, or whether it is due to a small impurity of the 1 - precursor 2 has still to be clarified). The generally accepted explanation of such a profound change in the emission spectra of porphyrins by the intramolecular presence of a quinoid system is the assumption of an electron-transfer from the porphyrin to the quinone [3]. Further spectroscopic investigations have been started to study more thoroughly the intramolecular electron-transfer in 1 which due to its well-defined and rather rigid molecular structure appears as a compound especially suited for such studies.

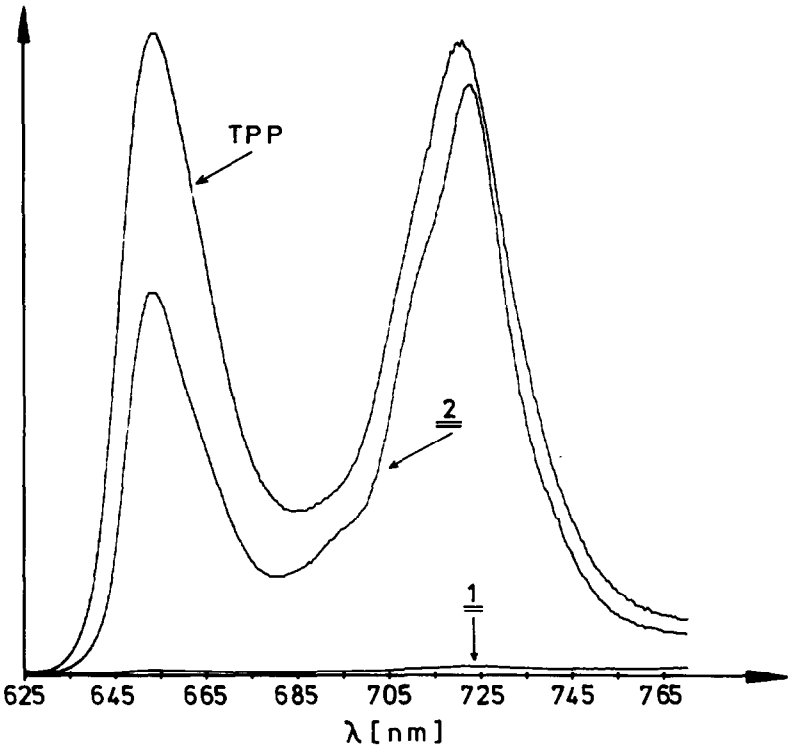

Figure 2. Fluorescence Spectra of 1 in Comparison with 2 and Tetraphenylporphyrin (TPP).

1) J. Weiser and H. A. Staab, Angew. Chem. 96, 602 (1984); Angew. Chem. Int. Ed. Engl. 23, 623 (1984); for list of references to recent contributions to this field see footnote 1.

2) D. J. Quimby, F. R. Longo, J. Am. Chem. Soc. 97, 5111 (1975).

3) L. V. Natarajan, R. E. Blankenship, Photochem. Photobiol. 37, 329 (1983); L. V. Natarajan, L. R. Humphreys, R. Chang, Spectrosc. Lett. 18, 219 (1985), and references therein.

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