

The Crystal Structure of Methylene Blue

By H. E. MARR III and J. M. STEWART*

(Chemistry Department, University of Maryland, College Park, Maryland 20742)

Summary The crystal structure of Methylene Blue hydrochloride pentahydrate reveals sheets of Methylene Blue molecules associated with chloride ions on the terminal nitrogens with a clathrate-like network of water molecules perpendicular to the planes formed by the phenazathionium units.

X-RAY diffraction studies of Methylene Blue have been undertaken several times, but the successful determination of the crystal structure has not been reported.^{1,2} We report the following information on the compound.

Crystal data: $[\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}]^+\text{Cl}^-\cdot 5\text{H}_2\text{O}$. Monoclinic; $a = 9.646(9)$, $b = 31.106(17)$, $c = 6.992(2)$ Å; $\beta = 96.70(6)^\circ$; $U = 2083.6$ Å³; $D_c = 1.306$, $D_m = 1.31$; $Z = 4$, space group $P2_1/c$ Mo- K_α radiation, niobium-filtered, single-crystal GE-XRD6 automated diffractometer.

The intensities of 2524 independent reflections were measured using the ω - 2θ scan technique. There were 1506 reflections observed to be significantly above background. The co-ordinates of the carbon, nitrogen, and sulphur atoms were obtained by direct methods. The rest of the structure was established by conventional Fourier techniques and the parameters of the structure were adjusted by full-matrix and block-diagonal least squares using the computing system for X-ray crystallography X-RAY67.³ The final conventional R factor is 0.057.

The hydrogen atom locations on the waters of hydration were confirmed with the aid of a proton-ordered tetrahedral model of the hydrogen-bonding network. This network is found in a narrow layer of water molecules which is perpendicular to the planes formed by the phenazathionium units.

The bond lengths indicate a partial quinoid structure

and suggest the charge is principally localized on the dimethylamino-groups. A further indication is that the chloride ion lies in the plane of the molecule nearest the dimethylamino nitrogen atoms and half way between symmetry-related molecules.

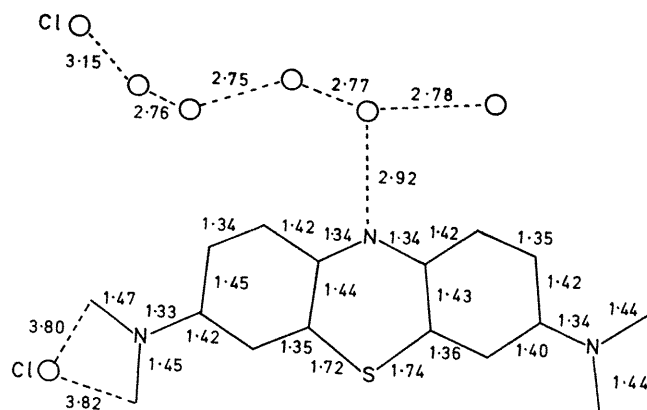


FIGURE. A schematic view of the dye molecule and its relationship in terms of bond distances to the chloride ions and five waters of hydration. All e.s.d.s less than 0.01 Å.

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¹ G. S. Zhdanov, Z. V. Zvonkova, and L. G. Vorontsova, *Kristallografiya*, 1956, **1**, 44.

² J. O. Warwick, *J. Chem. Soc.*, 1955, 2531.

³ XRAY67: "Program System for X-ray Crystallography." Computer Science Center, University of Maryland Technical Report 67-58, Dec. 1967.