The Dipole Moment of Pyocyanine

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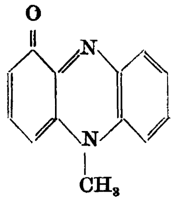
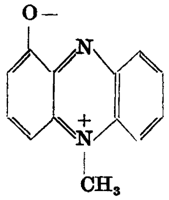
Pyocyanine, the blue colouring matter of the bacillus *Serratia marcescens (Bacillus pyocyaneus)* was shown by Wrede and Strack[1] to be an N-methyl derivative of 1-hydroxyphenazine and could be synthesized by treatment of 1-hydroxyphenazine with dimethyl sulphate. A bimolecular formula was originally assumed for pyocyanine, but the work of Michaelis[2], Elema[3] and Kuhn[4] established the monomolecular formula. Finally Hillemann[5] has shown that it is the nitrogen atom furthest away from the hydroxyl group which is methylated, so that a conventional formula for pyocyanine may be satisfactorily written as I.


I


II

The intense colour of pyocyanine, however, suggests that resonance structures of the type II may be of great importance for this compound, as are similar structures for the triphenylmethane and cyanine dyestuffs. Compounds of these types have been shown to possess very large dipole moments[6]. We have measured the dipole moment of pyocyanine, and found it also to be abnormally large.

Pyocyanine was prepared according to Surrey[7]. It was purified by dissolution in chloroform and precipitation with petroleum ether, when it had a melting point of 131–32°.

Pyocyanine is very slightly soluble in the solvents usually employed for dipole moment measurements. We only succeeded in making measurements in dioxane solutions, and even in this solvent the solubility was so low, that only an approximate value of the dipole moment could be determined.

The dielectric constants of dioxane and the solutions were measured, and the molecular polarization was measured, using the formula:

$$P_M = \frac{1000}{c}\left[\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right]$$

where c is the molar concentration of the solute and ε_1 and ε_{12} are the dielectric constants of the solvent and the solution (*cf.* Jensen and Nygaard[8]). The dipole moment was calculated from the formula:

$$\mu = 0.01273 \sqrt{P_M \cdot T}$$

The following values were obtained:

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c	$\Delta\varepsilon$	$\varepsilon^{25}_{\text{Dioxane}}$	P_M	μ
0.00415	0.0247 ± 0.0005	2.2103	1000 ± 20	7.0 D
0.00208	0.0130 ± 0.0005		1058 ± 40	
0.00104	0.0065 ± 0.0005		1058 ± 80	

The accuracy with which P_M can be determined in these very dilute solutions is too small to allow any reliable extrapolation to zero concentration. The solutions measured are, however, so dilute that P_M has probably already reached its maximum value. The true dipole moment can therefore not be much larger than 7.0 D, the value calculated from P_M of the most concentrated solution.

As expected the dipole moment of pyocyanine is rather large, showing that a highly dipolar structure plays an important rôle in determining the actual state of the molecule. Although there are other possible dipolar resonance structures, the only one of importance is probably that pictured as II. On the basis of the known bond lenghts and valency angles, a dipole moment of approximately 24 D can be calculated for this structure. Since the dipole moment of the single bond C—N is only small, the dipole moment of the ortho quinoid structure I should be almost exclusively determined by the moments of the bonds $>C = O$ and $>C = N-$. The first is about 2.5 D and the second is 1.6 D[9], so that the dipole moment of structure I may be taken as $\sqrt{2.6^2 + 1.6^2 + 2.6 \times 1.6} = 3.6$ D. If is assumed that the resulting dipole moment can be calculated from the formula[10]:

$$\mu = (1 - x_{II})\mu_I + x_{II}\mu_{II}$$

where μ is the dipole moment found and μ_I and μ_{II} are the moments calculated for structure I and II, the fractional contribution of the polar structure should be $x_{II} = 0.17$.

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The Dipole Moment of Sempervirine

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According to Prelog[1] sempervirine, the brown alkaloid of *Gelsemium sempervirens*, has the structure I. Woodward and Witkop[2], however, have presented evidence in favour of describing the molecule in terms of a resonance hybrid of structures II and III. This proposal accounts very well for the chemical and physical properties of sempervirine, but it remains to be shown that sempervirine has the high dipole moment required, if structure III makes a significant contribution to the state of the molecule.