Fluorescence Quantum Yields of 2-Substituted 3-Methylquinoxalines in Liquid Solutions at Room Temperature

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A sensitivity modulation method was employed to measure the fluorescence spectra and quantum yields of weakly fluorescent 2-substituted (NH₂, O, OCH₃, Cl, Br) 3-methylquinoxalines in n-hexane and methanol at room temperature. A strong decrease in the quantum yield with increasing atomic weight of the substituents was observed in n-hexane. In polar solvents, the Cl substituent is the strongest quencher although its atomic weight is 2.254 times smaller than that of Br.

1. Introduction

As evidenced by previous investigations on 2-substituted (NH₂, O, OCH₃, Cl, Br) 3-methylquinoxalines in polyvinyl alcohol (PVA) films [1], both fluorescence and phosphorescence occur simultaneously at room temperature, and their quantum yields are markedly different. A distinct effect of heavy atom substituents on the luminescent properties was observed for 3-methylquinoxalines, particularly for the –Cl and –Br substituents. For the –Br substituent, being 2.254 times heavier than Cl, in PVA at 293 K a weak fluorescence has been observed with a very low quantum yield of 0.008.

Amongst numerous mono- and disubstituent quinoxaline derivatives examined in various liquid solvents only few are fluorescing [2]. This is due to a strong spin-orbit coupling between the singlet and triplet states [3].

By the employment of a highly sensitive modulation method we were able to demonstrate that the above 2-substituted 3-methylquinoxalines display weak fluorescence in liquid solutions. In the present paper, the fluorescence spectra and quantum yields of the above substances in n-hexane and methanol are reported.
A. Kawski et al. • Fluorescence Quantum Yields of 2-Substituted 3-Methylquinoxalines

Fig. 1. Normalized absorption and fluorescence spectra of 2-substituted (NH₂, O, OCH₃, Cl, Br) 3-methylquinoxalines in n-hexane (1) and methanol (2).

Table 1. Fluorescence quantum yields, Φ_F, for 2-substituted 3-methylquinoxalines at room temperature.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Φ_F</th>
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<tbody>
<tr>
<td>-NH₂</td>
<td>0.01700</td>
</tr>
<tr>
<td>-O</td>
<td>0.00920</td>
</tr>
<tr>
<td>-OCH₃</td>
<td>0.00150</td>
</tr>
<tr>
<td>-CI</td>
<td>0.01100</td>
</tr>
<tr>
<td>-Br</td>
<td>0.00017</td>
</tr>
</tbody>
</table>

Quinine sulfate (0.5 mol dm⁻³ H₂SO₄) [5, 6] was used as standard in the determination of the fluorescence quantum yields for the substituents -NH₂, -OCH₃ and -O in n-hexane and methanol and for -Br in methanol, whereas for the substituent -Cl in methanol, hexane, diethylether, acetonitrile, ethyl acetate and for -Br in hexane and acetonitrile, the yield was determined relative to that for -Br in methanol (2 x 10⁻³, Table 1). The replacement of the standard was in this case imposed by the incapability of carrying out simultaneous measurements under identical geometrical conditions (without changing the monochromator slits) that should be preserved for the substances investigated and for quinine sulfate. A standard with a lower quantum yield should therefore be used. The quantum yield determination is significantly affected by the accuracy in the estimation of the surface area under the emission curves. Here, the signal-

\[
\Phi_F = \Phi_s \frac{\int I(\nu) \, d\nu}{\int I_s(\nu) \, d\nu} \left( \frac{1 - 10^{-D_s}}{1 - 10^{-D}} \right) \frac{n^2}{n_s^2},
\]

where Φ_s is the fluorescence quantum yield of a standard substance, D and D_s are optical densities, n and n_s are the refractive indices, respectively.
to-noise ratio, amounting to 8% in the case of the lowest yields, is a particularly important factor. The areas were calculated by numerical methods with an error of about 1%. An additional obstacle in the measurement of quantum yields of the order of $10^{-4}$ was the Raman scattering which was frequently comparable to the fluorescence of the compounds. Figure 1 shows the normalized longwave absorption and fluorescence spectra measured in n-hexane and methanol at 293 K. The quantum yields, $\Phi_F$, are summarized in Table 1. For the substituents –Cl and –Br, the quantum yields were also measured in the following polar solvents:

for –Cl in
- dichloroethane $\Phi_F = 0.00020$,  
- n-butyl acetate $\Phi_F = 0.00014$,  
- ethyl acetate $\Phi_F = 0.00015$,  
- diethylether $\Phi_F = 0.00022$,  
- acetonitrile $\Phi_F = 0.00022$, and

for –Br in
- acetonitrile $\Phi_F = 0.002$.

Table 1 shows that in n-hexane (nonpolar solvent) the fluorescence quantum yield decreases strongly when increasing the atomic weight of the substituent, whereas in the polar methanol solvent no regularity has been found, substituent –Cl, though considerably lighter than –Br, quenching the fluorescence by one order of magnitude more strongly. The behaviour of –Cl is similar in other polar solvents such as, for example, acetonitrile. Meanwhile, in rigid PVA the behaviour of the fluorescence quantum yield of –Cl at 293 K was similar to that in nonpolar n-hexane.