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 (NH_2, O, OCH_3, 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

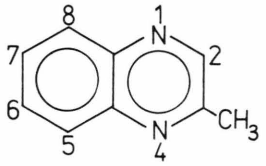
As evidenced by previous investigations on 2-substituted (NH_2, O, OCH_3, Cl, Br) 3-methylquinoxalines in polyvinyl alcohol (PVA) films [1], both fluorescence and phosphorescence occur simultaneously at room temperature, and their quantum yields are markedly different. A distinct effect of heavy atom 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 disubstituented quinoxaline derivates 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.

2. Experimental and Results

2-Substituted 3-methylquinoxalines:



$-NH_2$, $=O$, $-OCH_3$, $-Cl$ and $-Br$

where purified by recrystallization and vacuum sublimation.

The absorption spectra were measured on an M-40 (Carl Zeiss) spectrometer and the fluorescence spectra were recorded using a fully automatic spectrofluorimeter designed and built in our laboratory [4]. In the detection path of this apparatus two nanovoltmeters (one selective and one homodyne) and an FEU-79 photomultiplier operating in a single-photon regime (2200 V feed) were used. In our detection mode (frequency and phase-sensitive) both the excitation light from a xenon lamp and the emission from the substances examined were modulated by means of two synchronous choppers fed with a frequency of 40 Hz from a power generator. Low quantum yields (of the order of 10^{-4}) could be measured following a several hours warm-up of the whole apparatus. This essentially influenced the signal-to-noise ratio.

Fluorescence quantum yields, Φ_F, were determined relative to that of a standard substance according to

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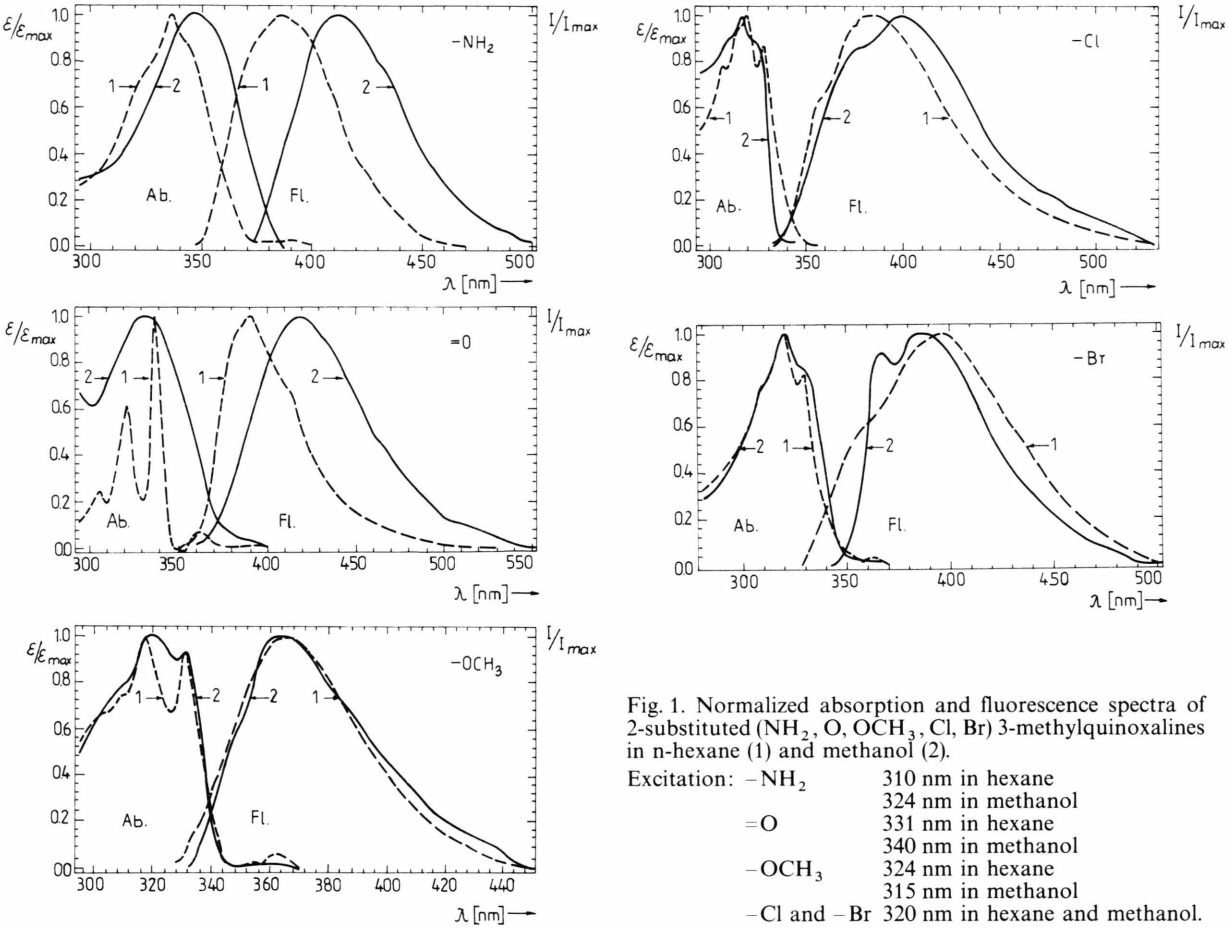

Fig. 1. Normalized absorption and fluorescence spectra of 2-substituted (NH_2, O, OCH_3, Cl, Br) 3-methylquinoxalines in n-hexane (1) and methanol (2).

Excitation:		
$-NH_2$	310 nm in hexane	
	324 nm in methanol	
$=O$	331 nm in hexane	
	340 nm in methanol	
$-OCH_3$	324 nm in hexane	
	315 nm in methanol	
$-Cl$ and $-Br$	320 nm in hexane and methanol.	

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

Solvent	Φ_F				
	$-NH_2$	$=O$	$-OCH_3$	$-Cl$	$-Br$
n-Hexane	0.01700	0.00920	0.00150	0.00017	0.00009
Methanol	0.07000	0.01100	0.01600	0.00023	0.00210

the relation

$$\Phi_F = \Phi_s \frac{\int\limits_0^\infty I(\tilde{\nu})\,d\tilde{\nu}}{\int\limits_0^\infty I_s(\tilde{\nu})\,d\tilde{\nu}} \left(\frac{1-10^{-D_s}}{1-10^{-D}}\right) \frac{n^2}{n_s^2}, \qquad (1)$$

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.

Quinine sulfate (0.5 mol dm^{-3} H_2SO_4) [5, 6] was used as standard in the determination of the fluorescence quantum yields for the substituents $-NH_2$, $-OCH_3$ 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 (2×10^{-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-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, Φ_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.

[1] Z. Gryczyński and A. Kawski, Z. Naturforsch. **46a,** 304 (1991).
[2] H. H. Perkampus, Z. Naturforsch. **17a,** 614 (1962).
[3] S. P. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall, Englewood Cliffs, New York 1969.
[4] A. Kawski and K. Nowaczyk, Acta Phys. Polon. **A 78,** 379 (1990).
[5] W. H. Melhuis, J. Phys. Chem. **65,** 229 (1961).
[6] Olmsted, J. Phys. Chem. **83,** 2581 (1979).