Substituent Effects on the Luminescence of 2-Substituted 3-Methylquinoxalines in Poly(Vinyl Alcohol) Films *

Z. Gryczyński and A. Kawski
Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Poland

Z. Naturforsch. **46a**, 304–306 (1991); received November 2, 1990

The effect of 2-substitutions (NH_2, O, CH_3O, Cl, Br) in 3-methylquinoxalines on the fluorescence and phosphorescence band position and intensity at 293 K, and the temperature dependence of their fluorescence and phosphorescence quantum yields were investigated in poly(vinyl alcohol) films.

1. Introduction

The effect of substituents on luminescence (fluorescence and phosphorescence) behaviour of quinoxaline is of great importance in the investigations of radiative and radiationless transitions. These two processes depend on the magnitude of spin-orbit interaction between singlet and triplet states, and on the transition moment between states of equal multiplicities [1]. The investigations of the heavy-atom substituent effect on the phosphorescence properties of frozen solutions of 2,3-disubstituted quinoxalines in different solvents (hexane, cyclohexane, methylcyclohexane, ethyl ether, isopentane), and in single crystals, have already been reported [2–5]. Recently, the effect of 5- and 6-substitutions on phosphorescence properties was investigated at low temperatures [6].

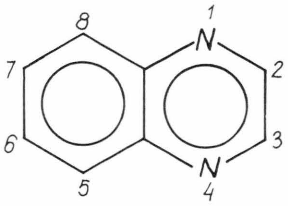
From amongst numerous mono- and disubstituted quinoxaline derivatives investigated in different solvents at room temperature (e.g., in n-hexane, n-heptane, methanol), only few emitted fluorescence. Readily measurable fluorescence was observed by Perkampus [7] for 2,3-dimethyloxy-quinoxaline and 2,3-diisopropoxy-quinoxaline in n-hexane and methanol.

2-Substituted 3-methylquinoxalines investigated in the present work by a highly sensitive modulation method of measuring the fluorescence spectra, exhibit weak fluorescence with a quantum yield ranging from 10^{-3} to 10^{-4} in n-hexane and methanol. However, when in rigid medium of polyvinyl alcohol (PVA) at room temperature, these compounds emit both fluorescence and phosphorescence markedly differing in the quantum yields.

The goal of the work reported here consisted in the investigation of the effect of 2-substituted (NH_2, O, CH_3O, Cl, Br) 3-methylquinoxalines in PVA on the position and intensity of fluorescence and phosphorescence bands at 293 K, and the temperature effect (from 80 to 333 K) on their fluorescence and phosphorescence quantum yields.

2. Experimental

2,3-Disubstituted quinoxalines:



2-amino-3-methylquinoxaline	(NH_2),
2-oxy-3-methylquinoxaline	(O),
2-methoxy-3-methylquinoxaline	(OCH_3),
2-chloro-3-methylquinoxaline	(Cl) and
2-bromo-3-methylquinoxaline	(Br)

were purified by recrystallization and vacuum sublimation.

Isotropic films were prepared of a 15% aqueous solution of polyvinyl alcohol (PVA) in which the molecules investigated were set up by methanol. The method of obtaining the films was described previously [8, 9]. Absorption spectra were measured on an M-40 (C. Zeiss, Jena) spectrophotometer, and the fluores-

---

* This work was carried out under the Polish Central Program for Fundamental Research CPBP 0.106.

Reprint requests to Prof. Dr. Alfons Kawski, Uniwersytet Gdański, Instytut Fizyki Doświadczalnej, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

0932-0784 / 91 / 0400-0304 $ 01.30/0. – Please order a reprint rather than making your own copy.

cence and phosphorescence* spectra were recorded using a fully automatic spectrofluorimeter designed and built in our institute [10, 11].

Fluorescence and phosphorescence quantum yields, $\Phi_{F,P}$, were determined relative to quinine sulfate in 0.5 mol dm^{-3} H_2SO_4 as a standard [12, 13], according to the relation

$$\Phi_{F,P} = \Phi^S \frac{\int_0^\infty J(\tilde{\nu})\,d\tilde{\nu}}{\int_0^\infty J^S(\tilde{\nu})\,d\tilde{\nu}} \left(\frac{1-10^{-D^S}}{1-10^{-D}}\right)\left(\frac{n}{n^S}\right)^2\left(\frac{2-r_n^S}{2-r_n}\right), \tag{1}$$

where Φ^S is the fluorescence quantum yield of a reference (standard) substance, D and D^S are optical densities, n and n^S are the refractive indices and r_n and r_n^S are the emission anisotropies of the sample and the standard, respectively, upon excitation by unpolarized light. The fluorescence anisotropy of quinine sulfate in 0.5 mol dm^{-3} H_2SO_4 is $r_n^S \cong 0$. The integrals represent the surface areas under the spectra of the sample and of the standard compound. The samples and the reference solution were excited at $\lambda_{exc} = 330$ nm (30303 cm^{-1}).

The measurements were carried out in a vacuum cryostat, the temperature being stabilized with an accuracy of ±1 K.

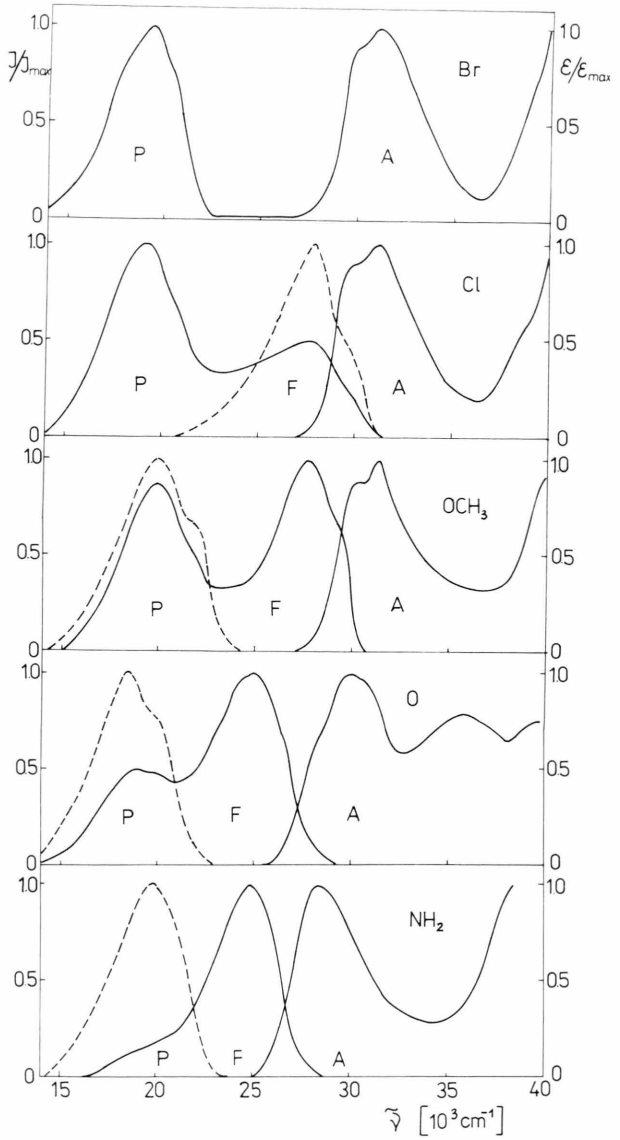


Fig. 1. Normalized absorption (A), fluorescence (F), and phosphorescence (P) spectra of 2-substituted (NH_2, O, OCH_3, Cl, Br) 3-methylquinoxalines in PVA films at 293 K.

3. Results and Discussion

The absorption, fluorescence, and phosphorescence spectra shown in Fig. 1 for 2-substituted 3-methylquinoxalines investigated in PVA at 293 K do not display vibrational structure and are broadened. The effect of heavy atoms substituted in position 2 is clearly noticeable. A distinct effect of substituents on the absorption, fluorescence, and phosphorescence band positions is particularly observed in the case of light substituents, such as NH_2 and O. For the heavy substituents Cl and Br, the absorption and fluorescence spectra overlap entirely. The strongest fluorescence in PVA is emitted at room temperature for the substituent NH_2. In this case, a weak phosphorescence band can hardly be observed around 20 kK. The phosphorescence band enhances distinctly for substituent O, despite equal atomic weights of these substituents (NH_2 and O). The heavy atom effect is markedly stronger for OCH_3. The quantum yields measured for the substances investigated as a function of temperature have been summarized in Table 1. As can be inferred based on the results given therein, the relative phosphorescence to fluorescence quantum yield, Φ_P/Φ_F, at 293 K increases in the presence of heavy atom: the respective quantum yield ratios for NH_2, O, and OCH_3 amount to 0.057, 0.438, and 0.784. The ratio Φ_P/Φ_F increases distinctly for markedly heavier atoms, Cl and Br, amounting to 2.423 and 21.63, respectively (Table 1). For Cl substituent, which is only slightly heavier than OCH_3, the

---

* By "phosphorescence" we mean the emission due to the radiative transition from the lowest triplet state T_1 to the ground state S_0 of the molecule.

Table 1. Fluorescence Φ_F and phosphorescence Φ_P quantum yields as function of the temperature T for 2-substituted 3-methylquinoxalines.

2-substitution / T (K)	NH_2		O		OCH_3		Cl		Br	
	Φ_F	Φ_P	Φ_F	Φ_P	Φ_F	Φ_P	Φ_F	Φ_P	Φ_F	Φ_P
333	0.180	0.001	0.030	0.001	0.040	0.002	0.018	0.003	0.006	0.006
313	0.195	0.002	0.050	0.003	0.050	0.007	0.020	0.008	0.007	0.040
303	0.200	0.006	0.058	0.014	0.070	0.023	0.025	0.031	0.008	0.102
293	0.210	0.012	0.064	0.028	0.074	0.058	0.026	0.063	0.008	0.173
283	0.210	0.032	0.067	0.035	0.075	0.097	0.028	0.124	0.008	0.262
273	0.214	0.064	0.072	0.042	0.077	0.153	0.031	0.271	0.008	0.360
263	0.218	0.097	0.077	0.052	0.079	0.241	0.032	0.322	0.008	0.480
253	0.220	0.120	0.080	0.061	0.081	0.356	0.033	0.397	0.008	0.602
233	0.223	0.161	0.089	0.084	0.085	0.480	0.038	0.542	0.008	0.741
173	0.252	0.238	0.100	0.108	0.118	0.700	0.043	0.767	0.008	0.904
100	0.264	0.254	0.128	0.140	0.121	0.772	0.044	0.886	0.009	0.922
80	0.271	0.260	0.137	0.148	0.122	0.786	0.044	0.891	0.009	0.922

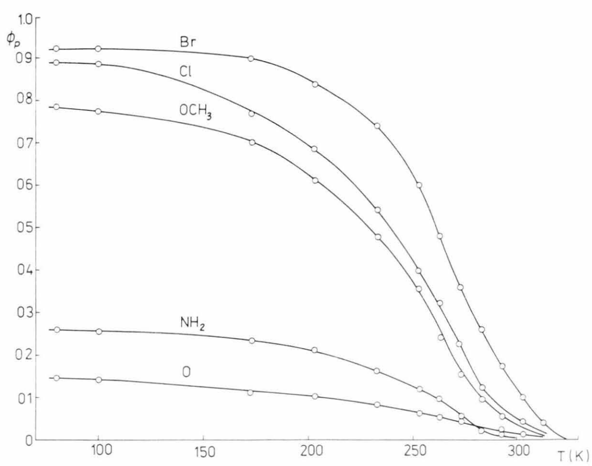


Fig. 2. Effect of temperature on the phosphorescence quantum yield Φ_P, of 2-substituted 3-methylquinoxalines in PVA films.

increase in Φ_P/Φ_F is not high, amounting to 2.423, whereas for Br, heavier than Cl by 2.254, fluorescence cannot practically be observed (Fig. 1, Br). In this case, the fluorescence quantum yield at 293 K scarcely amounts to 0.008.

Upon descreasing the temperature, an enhancement both in the fluorescence and phosphorescence quantum yields is observed for the substituents NH_2, O, and OCH_3. At 80 K, the ratio Φ_P/Φ_F amounts to 0.959, 1.080, and 6.443 for NH_2, O, and OCH_3, respectively. Φ_P/Φ_F enhances rapidly at 80 K for Cl and Br, amounting to 20.25 and 102.4, respectively (Table 1), thus evidencing the heavy atom effect and, hence, considerable spin-orbit interaction between the singlet and triplet states. The behaviour of the phosphorescence quantum yield, Φ_P, as a function of temperature is shown in Fig. 2 for all compounds investigated. In the temperature range of 80 K – 100 K, Φ_P can be considered as almost temperature-independent.

Acknowledgements

The authors wish to thank Professor E. Lippmann (Sektion Chemie der Universität Leipzig) for his kind gift of quinoxaline derivatives.

[1] S. P. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall, Englewood Cliffs, New York 1969.
[2] D. S. Tinti and M. A. El-Sayed, J. Chem. Phys. **54,** 2529 (1971).
[3] H. Ishii, Y. Murakami, R. Shimada, and Y. Kanda, Memoirs Fac. Sci., Kyushu Univ. Ser. C **9,** 189 (1975).
[4] S. Yamauchi and T. Azumi, J. Chem. Phys. **68,** 4138 (1978).
[5] K. Suga and M. Kinoshita, Bull. Chem. Soc. Japan **55,** 1695 (1982).
[6] A. Lewanowicz, J. Lipiński, Z. Ruiewicz, A. Szymczak, and J. Szynkarczuk, J. Luminesc. **43,** 85 (1989).
[7] H. H. Perkampus, Z. Naturforsch. **17a,** 614 (1962).
[8] Y. Tanizaki, .T. Kobayashi, and N. Ando, Bull. Chem. Soc. Japan **32,** 119 (1959).
[9] A. Kawski, in: Optical Spectroscopy in Chemistry and Biology – Progress and Trends (D. Fassler, ed.), VEB Deutscher Verlag der Wissenschaften, Berlin 1989, pp. 135–153.
[10] A. Kawski, J. Kamiński, and E. Kuteń, J. Phys. B **4,** 609 (1971).
[11] A. Kawski and K. Nowaczyk, Acta Phys. Polon. **A 78,** 33 (1990).
[12] W. H. Melhuish, J. Phys. Chem. **65,** 229 (1961).
[13] J. Olmsted, J. Phys. Chem. **83,** 2581 (1979).
[14] R. C. Hirt, F. T. King, and J. C. Cavagnol, J. Chem. Phys. **25,** 574 (1956).
[15] K. Brenner and Z. Ruziewicz, J. Luminesc. **15,** 235 (1977).