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Emission and absorption spectra of some substituted 4-hydroxypyrimidines

D. SEN and C. H. J. WELLS
School of Chemical and Physical Sciences, Kingston Polytechnic, Kingston upon Thames, Surrey KT1 2EE, U.K.

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Abstract—The fluorescence, phosphorescence and absorption spectra of 5,6-dimethyl-2-dimethylamino-4-hydroxypyrimidine (1), 5-*n*-butyl-2-dimethylamino-4-hydroxypyrimidine (2), and 5-*n*-butyl-2-ethylamino-4-hydroxypyrimidine (3) have been obtained in organic media and in aqueous solution at different pH values. The spectra reveal that the pyrimidines exist principally as cations at low pH, neutral species at pH values around 7 and as anions at high pH. The p*K* values for the ground state of compounds (1)–(3) have been measured as have the pK^* values for the first excited singlet state.

INTRODUCTION

The photochemical behaviour of the pyrimidines thymine (2,4-dihydroxy-5-methylpyrimidine) and uracil (2,4-dihydroxypyrimidine) is of great interest because of the role these pyrimidines play in the photodenaturation of nucleic acids [1–5]. As a consequence of this role, the spectroscopic properties of these and related compounds have been well documented [2,5–10]. The structural relationship of 5,6-dimethyl-2-dimethylamino-4-hydroxypyrimidine (1), 5-*n*-butyl-2-dimethylamino-4-hydroxypyrimidine (2) and 5-*n*-butyl-2-ethylamino-4-hydroxypyrimidine (3) to the nucleic acid pyrimidines has evoked interest in their photochemistry [11, 12], especially as compounds (2) and (3) are used as systemic fungicides [13, 14]. Knowledge of the photochemical behaviour of compounds (1)–(3) is of value because of the likelihood of photochemical reactions occurring when they are exposed to sunlight under field conditions. In order to gain information on possible species involved in the photochemistry of compounds (1)–(3), their emission and absorption spectra have been investigated and the results are reported herein.

EXPERIMENTAL

Compounds (2) and (3) were supplied by the Plant Protection Division, I.C.I. Ltd., and were recrystallized twice from methanol prior to use. Compound (1) was prepared by an adaptation of the method of HULL *et al.* [15]. 1,1-Dimethylguanidine sulphate (27.2 g) was added to ethanolic sodium ethoxide, prepared by adding clean sodium (4.6 g) to redistilled absolute ethanol (150 cm^3). The mixture was shaken for 15 min., then ethyl-2-methylacetoacetate (28.8 g) was added and the solution allowed to stand for 18 h, after which time it was refluxed for 2 h, cooled, filtered and the filtrate evaporated to low volume, whence compound (1) crystallized as needles. Recrystallization from methanol yielded product (8.4 g), m.p. 169–173°.

Fluorescence and phosphorescence spectra were recorded using a Perkin–Elmer/Hitachi MPF4 spectrometer. U.v. absorption spectra were recorded using a Unicam SP8000 spectrophotometer. Absorbance measurements were made using a Pye–Unicam SP6-500 and Perkin–Elmer Coleman 55 spectrometer. The u.v. absorption spectra were obtained at various pH values in triple distilled water and in a number of non-aqueous solvents. The pH values of the solutions were adjusted using 1 or 0.1 M hydrochloric acid (Hopkins and Williams, volumetric), and 1 or 0.1 M sodium hydroxide (Hopkins and Williams, volumetric). The spectra were recorded immediately after adjustment of pH and the pH of the solutions were measured before and after recording the spectra and an average pH value thus obtained.

RESULTS AND DISCUSSION

Data for the wavelength of maximum fluorescence and phosphorescence emission of compounds (1)–(3) are listed in Table 1. It can be seen from the table that for all three compounds the λ_{max} values

Table 1. Wavelength maxima (λ_{max}) for fluorescence and phosphorescence emission

Compound	pH	Fluorescence* λ_{max} (nm) 77 K†	Fluorescence* λ_{max} (nm) 298 K†	Phosphorescence‡ λ_{max} (nm) 77 K§
1	1.91	388	387	
	4.32	365	372	435
	5.51	360	365	
	7.00	358	365	430
	8.92	350	360	
	10.11	350	356	420
	11.64	350	356	
	13.40	350	360	
2	1.91	385	385	
	4.32	385	375	430
	5.51	380	370	
	7.00	375	365	425
	8.92	375	365	
	10.11	375	362	415
	11.64	375	362	
	13.40	360	360	
3	1.91	360	365	
	4.32	360	360	430
	5.51	355	360	
	7.00	355	358	430
	8.92	365	358	
	10.11	365	360	415
	11.64	365	356	
	13.40	335	356	

* Solvent—water.
† Excitation wavelength—290 nm.
‡ Solvent—ethylene glycol : water (1 : 1 v/v).
§ Excitation wavelength—300 nm.

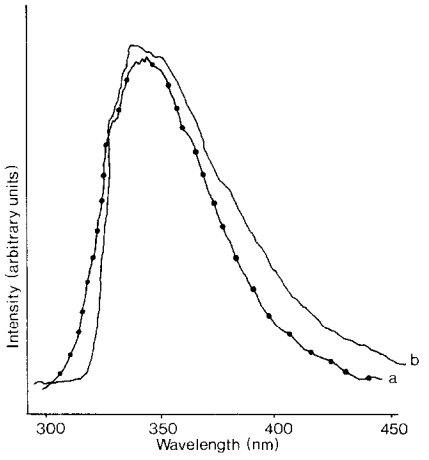


Fig. 1. Fluorescence spectra of compound (1) at 77 K in: (a) cyclohexane : isopentane (1 : 5 v/v), and (b) aqueous solution at pH = 7.02.

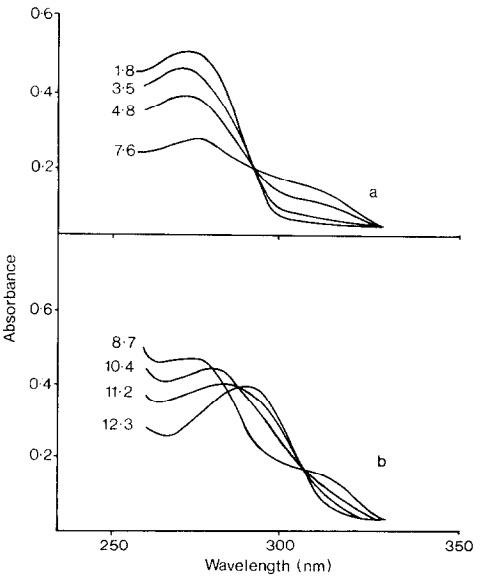


Fig. 2. Absorption spectra of compound (1) (0.96×10^{-3} M) in aqueous solution over pH ranges: (a) 1.8–7.6, and (b) 8.7–12.3.

for fluorescence and phosphorescence decrease as the pH increases, indicating that different species are acting as principal emitters in different pH regions. The bathochromic shift of the fluorescence λ_{max} values when the temperature is changed from 77 to 298 K is consistent with previous observations on the fluorescence spectra of nucleic acid pyrimidines [2].

The fluorescence spectrum of compound (1) in aqueous solution at pH = 7.02 is shown in Fig. 1, along with the fluorescence spectrum in cyclohexane : isopentane. The close similarity between the fluorescence spectra in the two solvent media, which was also observed for the fluorescence emission of compounds (2) and (3), is paralleled by the close similarity between the phosphorescence spectra of these compounds in ethylene glycol : water at pH = 7.00 and in cyclohexane : isopentane. These observations suggest that for each of the compounds the same species is emitting in the protic and aprotic solvent systems. Since it is unlikely that these pyrimidine compounds would be present in any form other than a neutral molecule in an aprotic solvent system such as cyclohexane : isopentane, it may be concluded that these pyrimidines exist mainly as neutral species in aqueous solution at pH values close to 7.

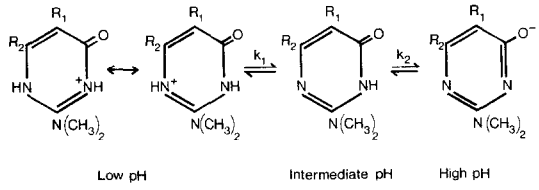
The u.v. absorption spectra of compound (1) at different pH values are shown in Fig. 2. Similar spectra were obtained for compounds (2) and (3). The figure shows that over the low pH range there is an isosbestic point at 290 nm whilst over the high pH range there is an isosbestic point at 309 nm. These observations taken in conjunction with the observations on the fluorescence and phosphorescence spectra indicate the existence of two single equilibria in the low and high pH ranges. This is explainable in terms of a cationic pyrimidinol species being present at low pH and an anionic pyrimidinol species at high pH with these species being in equilibrium with the neutral pyrimidinol

Table 2. Spectral and ionization data

Compound	pH	Species	λ_{max} (nm)	ε ($cm^2\ mol^{-1}$)	Isosbestic points (nm)	Ground state pK_1†	Ground state pK_2†	First excited singlet state pK_1^*‡	First excited singlet state pK_2^*‡
1	1.00	Cation	270	79,200	290	4.19	10.13	3.13	8.69
	7.00	Neutral	275 (298§)	4850					
	12.00	Anion	290	6670	309				
2	1.00	Cation	272	79,500	291	4.60	10.79	3.86	9.55
	7.00	Neutral	277 (300§)	5010					
	13.00	Anion	290	6650	305				
3	1.00	Cation	269	79,500	285	4.46	10.72	5.21	10.05
	7.00	Neutral	276 (296§)	4910					
	12.10	Anion	283	6630	299				

† Determined by the method described by ALBERT and SERJEANT [16].
‡ Determined by the method described by WELLER [17] and VANDER DONCKT [18].
§ Inflection point.

which is itself the principal species present at intermediate pH values. The equilibria may be represented as shown in the following scheme



The absorption maxima and molar extinction coefficients of the cationic, anionic and neutral pyrimidinols are listed in Table 2. Also listed in the table are the ground state pK values for the equilibria shown in the scheme, along with the pK^* values for the equilibria when involving first excited singlet state molecules. As expected, there are relatively small differences in the ground state pK values of compounds (1)–(3), reflecting the minor structural differences between these compounds. It is of interest that the pK^* values of the first excited singlet state of compounds (1)–(3) are generally less than the corresponding ground state pK values. Thus, compounds (1)–(3) act as weaker bases in their first excited singlet state than in the ground state and this may be an important factor in relation to their photochemistry when these pyrimidines are excited into their singlet state manifold.

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REFERENCES

[1] J. G. BURR, *Adv. Photochem.* **6,** 193 (1968).
[2] R. F. STEINER and I. WEINRYB, *Excited States of Proteins and Nucleic Acids*, Vols. 1 and 2, Macmillan, London (1971).
[3] A. J. VARGHESE, *Photophysiology* 207 (1972).
[4] D. W. WHILLANS and H. E. JOHNS, *Curr. Top. Radiat. Res. Quart.* **9,** 119 (1973).
[5] G. J. FISHER and H. E. JOHNS, *The Photochemistry and Photobiology of Nucleic Acids*, Edited by S. Y. WANG, p. 169, Gordon & Breach, London (1976).
[6] D. SHUGAR and J. J. FOX, *Biochim. Biophys. Acta* **9,** 199 (1952).
[7] S. UNDENFRIEND and P. ZALTZMAN, *Analyt. Biochem.* **3,** 49 (1962).
[8] Y. KLEINWACHTER, J. DROBNIK and L. AUGENSTEIN *Photochem. Photobiol.* **5,** 579 (1966).
[9] A. FAVRE, *Photochem. Photobiol.* **19,** 15 (1974).
[10] A. G. SZABO and K. B. BERENS, *Photochem. Photobiol.* **21,** 141 (1975).
[11] B. D. CAVELL, S. J. POLLARD and C. H. J. WELLS, *Chem. Ind. (London)* 566, (1976).
[12] B. D. CAVELL, S. J. POLLARD and C. H. J. WELLS, *J. Chem. Soc. Perkin* II, 216 (1977).
[13] R. M. BEBBINGTON, D. H. BROOKS, M. J. GEOGHEGAN and B. K. SNELL, *Chem. Ind. (London)*, 1512 (1969).
[14] R. S. ELIAS, M. C. SHEPPARD, B. K. SNELL and J. STUBBS, *Nature* **219,** 1160 (1968).
[15] R. HULL, B. J. LOVELL, H. T. OPENSHAW, L. C. PAYMAN and A. R. TODD, *J. Chem. Soc.* 357 (1946).
[16] A. ALBERT and E. D. SERJEANT, *The Determination of Ionization Constants*, Chapman & Hall, London (1971).
[17] A. WELLER, *Prog. Reaction Kinetics* **1,** 189 (1961).
[18] E. VANDER DONCKT, *Prog. Reaction Kinetics* **5,** 273 (1970).