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SHORT COMMUNICATIONS

EFFECT OF ELECTRON DONATING SUBSTITUENTS ON THE ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTRA OF COUMARIN DERIVATIVES

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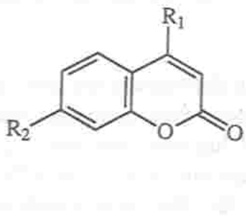
ABSTRACT. The electronic absorption and fluorescence spectra of eight coumarins substituted with electron-donating groups have been determined at 298 K in dioxane, ethyl ether, ethyl acetate, ethanol, acetonitrile, dimethylformamide, and dimethyl sulfoxide. Good linear correlations have been established between the maxima wave numbers of 0-0 electronic absorption or maxima of fluorescence and Hammett substituent constants. The electronic absorption and fluorescence spectra have been interpreted in terms of the decrease of the energy gap between the ground and the excited singlet states upon substitution of the coumarin.

INTRODUCTION

Coumarin (**1**) and its derivatives (**2-8**), constitute organic compounds which have stimulated interesting research in biology, medicine, photochemistry and spectroscopy [1-6].



	R_1	R_2
1	H	H
2	H	CH_3
3	H	OCH_3
4	OH	H
5	H	OH
6	CH_3	OH
7	CH_3	NH_2
8	CH_3	$N(CH_3)_2$

Wolbeis *et al.* [7], and Hammond and co-workers [8] have shown that the luminescent properties of coumarin derivatives are very sensitive to solvent, concentration, and temperature effects. Review articles have been published concerning the structure, pH and solvent effects of coumarins [9-12]. However, no systematic study on substituent effects have been conducted in luminescence spectroscopy.

In this paper we report the effect of electron donating substituents on the electronic absorption and fluorescence spectra of eight coumarin derivatives (**1 - 8**).

EXPERIMENTAL

Instrumentation. The electronic absorption spectra were recorded at 298 K with a Beckman model 3600 spectrophotometer and the emission fluorescence spectra were measured at the same temperature on a Pekin-Elmer L S - 5 spectrofluorometer.

Reagents. Analytical-grade solvents were used to prepare solutions. All solvents and chemicals were purchased from Aldrich.

Choice of the substituent constants. In order to examine quantitatively the effects of electron-donating substituents on the energy of electronic transitions, we have applied the classical Hammett treatment [13]. All substituents occupy the 4 or 7 position of the coumarin moiety. We have therefore utilized σ_p values for these substituents for which the existence of resonance as well as inductive interactions with the electron pair of the O_{11} oxygen can be assumed. For the coumarin derivatives having several substituents, we have utilized the algebraic sum of the respective σ_p values.

RESULTS AND DISCUSSION

Electronic absorption spectra. We have determined the electronic absorption spectra of coumarin derivatives in several protic and aprotic solvents. The absorption maxima are given in Table 1.

Generally three main absorption bands are observed in the 200-220 nm, 260-290 nm and 310-370 nm regions, depending on the solvent and the compound (Figure 1). All bands correspond to $\pi \rightarrow \pi^*$ electronic transition ($\epsilon = 10^3$ - 10^5 M^{-1} cm^{-1}). No $n \rightarrow \pi^*$ transition was observed. Nevertheless, the presence of shoulders for some of the derivatives can be ascribed to overlapping π-π^* and n-π^* bands. The latter ones are probably due to the presence of the carbonyl chromophore in the pyrone moiety.

The spectrum of 7-dimethyl amino-4-methyl coumarin has the same form as those of 7-amino coumarin derivatives. These electronic spectra have intense bands at the longest wavelengths corresponding to overlapping of many electronic transitions. Because of resonance, the spectra of the 7-amino coumarin derivative are more sensitive to solvent polarity.

Fluorescence spectra. Among the eight coumarin derivatives studied, only compounds **3-8** exhibited fluorescence. It is already known that coumarin itself exhibits no fluorescence, although a weak emission at 77 K has been reported [2].

The emission spectra of coumarins exhibit only one band in the 370-440 nm region, depending on the compound and solvent. The fact that most compounds exhibited a marked red shift of the florescence emission spectra, upon increasing the solvent polarity, is a further evidence of a $\pi^* \rightarrow \pi$ transition (Table 2, Figure 2) [14].

Effect of electron donating-substituents on the $S_0 \rightarrow S_1$ transitions. Table 1 shows that electron donating substituents exert a bathochromic shift on the 0-0 transition band of coumarins, thereby decreasing the $S_0 \rightarrow S_1$ transition energy.

The absorption maxima wave numbers ($\overline{\nu}_A$) of the 0-0 transition bands of substituted coumarins were plotted against the Hammett substituent constants according to equation 1.

$$\bar{\nu}_A = \rho\sigma + \bar{\nu}^o_A \tag{1}$$

where ρ is the Hammett reaction constant, $\bar{\nu}_A$ is the wave number of the 0-0 band absorption maximum of substituted coumarin and $\bar{\nu}^o_A$ is the wave number of the 0-0 band absorption maximum of the unsubstituted coumarin.

Table 1. Electronic absorption maxima wavelengths (nm) of coumarin derivatives in several solvents at 298 K*.

Compound	Dioxane	Ethyl ether	Ethyl acetate	Ethanol	DMF	Acetonitrile	DMSO
1	270 280 309	271 280 309	272 280 309	273 280 309	274 280 309	271 280 309	274 280 309
2	214 278 285 314	213 277 285 309	277 312	212 285 312	276 322 314	247 273 313	287 314
3	216 296 302 319	309 319	309 319	205 216 322	309 320	309 319	320
4	216 276 279 290 314	213 277 290 314	266 278 290 314	266 278 290 314	268 280 290 314	268 280 290 317	267 288 290 316
5	320	296 315	290 317	306 326	290 323	290 319	290 325
6	223 290 318	208 290 319	290 319	290 324	243 290 321	215 290 317	290 310 322
7	214 228 340	213 339	340	205 230 350	349	205 228 342	258 356
8	213 236 357	214 234 349	214 235 352	209 240 367	259 370	209 238 360	257 368

* The longest wavelengths represent 0-0 transition bands.

Table 2. Fluorescence maxima wavelengths (nm) of coumarin derivatives in different solvents at 298 K.

Compound	Dioxane	Ethyl ether	Ethyl acetate	Ethanol	DMF	Acetonitrile	DMSO
2	382	379	381	382	385	381	386
4	369	374	376	370	381	390	395
5	380	385	380	386	388	389	397
6	375	374	372	382	382	377	384
7	404	391	415	445	432	433	440
8	414	394	400	427	416	412	421

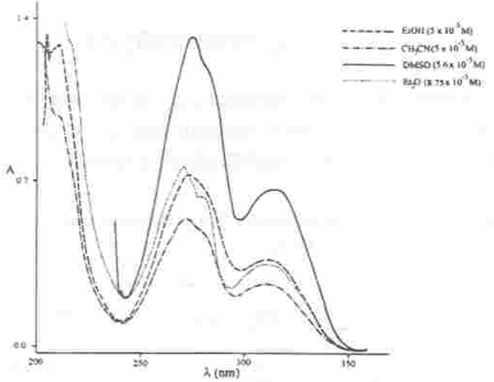


Figure 1. Electronic absorption spectra of coumarin in different solvents

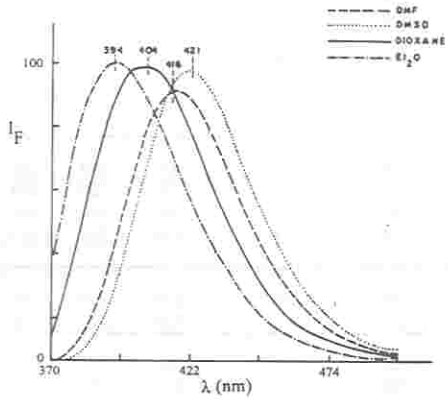


Figure 2. Fluorescence spectra of 7-amino-4-methyl coumarin (10^{-7} M) in different solvents.

We have obtained linear correlations between the wave numbers ($\bar{\nu}_A$) of the absorption maxima and Hammett substituent constants in all solvents, and for most coumarins studied (Table 3; Figure 2). We have found that correlation coefficient (r) values are larger than 0.94, suggesting that the Hammett linear free-energy relationships are established with a satisfactory precision for all solvents. The ρ values are relatively large, ranging between 3.8 and 5.4 K cm^{-1}, depending on the polarity of the solvent (Table 3).

Since the ρ values are positive, the ρσ product presents always a negative value (with $\sigma < 0$), that is $\bar{\nu}_A - \bar{\nu}_A^o < 0$ from equation 1. This implies that the values of $\bar{\nu}_A$ decrease strongly when the electron donating ability of substituents increase. This behavior suggests that the $S_0 \rightarrow S_1$ transition energy gap diminishes with substitution, which is typical of $\pi \rightarrow \pi^*$ transition [14].

Effect of electron donating substituents on the $S_1 \rightarrow S_0$ transition. Electron donating substituents shift the fluorescence maximum of coumarin to longer wavelength (Table 2 , Figure 3). Hence, such groups are expected to lower the energy of the singlet state relative to that of coumarin.

Table 3. Statistical treatment of the Hammett correlation of electronic absorption 0-0 band wave numbers of coumarin derivatives in several solvents

Solvent	Slope (cm^{-1})	Intercept (cm^{-1})	Correlation coefficient	Number of data
Dioxane	4174	32542	0,987	6
Ethyl ether	3851	32854	0,950	8
Ethyl acetate	3971	32813	0,945	7
Ethanol	4999	32675	0,969	7
DMF	5175	32934	0,941	8
Acetonitrile	4544	32793	0,967	7
DMSO	5473	32801	0,979	7

We have found that the fluorescence maxima wave numbers ($\bar{\nu}_F$) of most coumarins correlate linearly with the Hammett substituent constants (Table 4, Figure 4). The correlations are of the general form:

$$\bar{\nu}_F = \rho\sigma + \bar{\nu}_F^o \qquad (2)$$

where ρ is the fluorescence reaction constant, $\bar{\nu}_F$ and $\bar{\nu}_F^o$ are the wave numbers of the fluorescence maxima of substituted and unsubstituted coumarin, respectively.

We obtained positive ρ values for all solvents with r ranging between 0.93 and 0.99, which demonstrated that Hammett linear free-energy relationships are established with a satisfactory precision in all studied solvents. Since ρ values are positive, the ρσ product always presents a negative value (with $\sigma < 0$). It also confirms that the fluorescence transitions of these coumarin belong to $\pi \rightarrow \pi^*$ type [14].

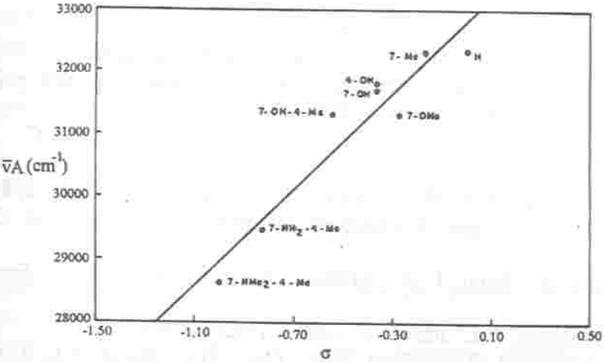


Figure 3. Correlation of wave number of the electronic absorption maxima of coumarin derivatives with Hammett substituent constants in ethyl ether.

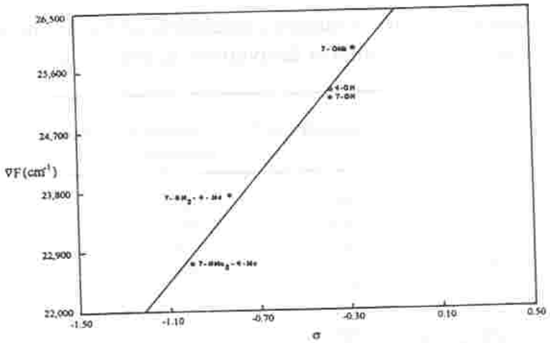


Figure 4. Correlation of wave numbers of the fluorescence maxima of coumarin derivatives with Hammett substituent constants in DMSO.

Table 4. Statistical treatment of the Hammett correlations of fluorescence maxima wave numbers of coumarin derivatives in several solvents.

Solvent	Slope (cm^{-1})	Intercept (cm^{-1})	Correlation Coefficient	Number of data
Dioxane	4279	28459	0,948	5
Ethyl ether	2451	27201	0,929	5
Ethyl acetate	3169	27450	0,967	5
Ethanol	5827	28479	0,937	5
DMF	4093	27348	0,981	5
Acetonitrile	3880	27182	0,986	5
DMSO	3794	26836	0,991	5

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