Quantitative study of the substituent effects on the electronic absorption and fluorescence spectra of coumarins

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Introduction

The fluorescence properties of coumarins are highly dependent on their molecular structure. Recent studies have demonstrated that substituted coumarin quantum fluorescence yields were related to the substituent type[1,2]. In this work, we have used the Hammett equation[3] to evaluate the substituent effects on coumarin absorption and fluorescence spectra.

Materials and Methods

UV absorption and fluorescence spectra were recorded using a Perkin-Elmer Lambda2 absorption and a LS-50 spectrofluorimeter at room temperature. We applied the Hammett equations: $\bar{\nu} = \rho\sigma + \bar{\nu}_0$. The carbonyl oxygen negative electronic charges Q and HOMO and LUMO energies were calculated by the AM1 method.

Results and discussion

The correlation ρ positive values of $\bar{\nu}$ vs. σ (Fig. 1) correspond to coumarin red-shifts absorption and fluorescence bands by electron-donor substituents and to blue-shifts of these bands by electron-acceptor substituents. Thus, the inductive and mesomeric electron-donor effects of C-7 NEt_2, NMe_2, NH_2, OH substituents reduce the energy gap between the S_0 and S_1 electronic states, while the inductive electron-acceptor effects of C-7 Cl and Br substituents increase the gap between both states. These results are in agreement with the AM1theoretical data based on the HOMO and LUMO energy calculations. Moreover, the Stokes shift decreases and increases, respectively observed for the electron-donor and for the electron-acceptor substituents, can be also explained by the Hammett correlations. The negative charge of the carbonyl oxygen underwent the influence of the C-7 substituents, which would explain the observed absorption and fluorescence bands shifts.

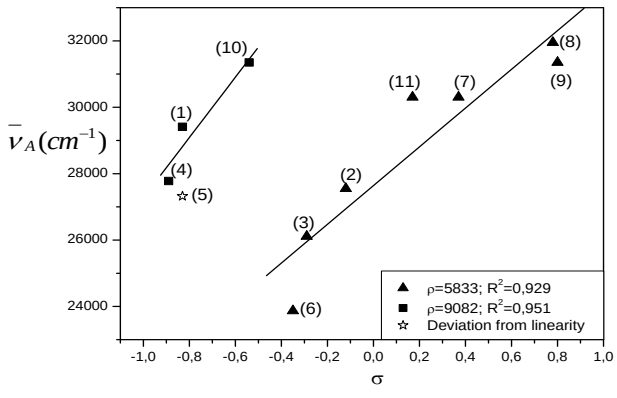

Fig. 1. Hammett plots of $\bar{\nu}_A$ vs. σ in 1,4-dioxan solvent. **(1)**7-amino-4-methylcoumarin; **(2)**7-amino-4-trifluoromethyl coumarin; **(3)**7-dimethylamino-4-trifluoromethylcoumarin; **(4)** 7-diethylamino-4-methylcoumarin; **(5)**7-diethylaminocoumarin-3-carboxylic acid; **(6)** 7-diethylaminocoumarin; **(7)**coumarin-3-carboxylic acid; **(8)**7-Cl-4 trifluoromethylcoumarin; **(9)**7-Br-4-trifluoromethylcoumarin; **(10)**7-OH-4-methyl coumarin; **(11)**7-OH-4-trifluoromethyl coumarin.

Conclusion

It exists linear correlations between the coumarin electronic spectral properties and Hammett substituent constants σ. The ρ positive values indicate that inductive and mesomeric electron-donor effects of the C-7 substituents decrease the $\bar{\nu}_A$, $\bar{\nu}_F$, $\bar{\nu}_A - \bar{\nu}_F$ and electronic charge Q values.

Bibliography

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