Estimation of ground- and excited-state dipole moments of 3-acetoacetyl-coumarin derivatives from a solvatochromic shift method based on the solvent polarity parameter

Malika Makhloufi-Chebli [a,b], Safouane M. Hamdi [c], Amal Rabahi [a], Artur M.S. Silva [d], Maamar Hamdi [a,*]

[a] *Laboratoire de Chimie Organique Appliquée, Faculté de Chimie, Université des Sciences et de la Technologie, BP32, El-Alia 16111 Bab-Ezzouar, Alger, Algérie*
[b] *Université Mouloud Mammeri, Faculté des Sciences, Département de Chimie, Tizi Ouzou, 15000, Algérie*
[c] *Laboratoire de Biochimie-Purpan, Institut Fédératif de Biologie, CHU Toulouse 3330, Avenue de Grande Bretagne-F-31039 Toulouse cedex 9, France*
[d] *Department of Chemistry & QOPNA, University of Aveiro, 3810-193, Aveiro, Portugal*

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ABSTRACT

The optical properties of **1** (3-acetoacetylcoumarin), **2** (3-acetoacetylbenzo[f]coumarin) and **3** (3-acetoacetylbenzo[h]coumarin) were investigated by UV/vis absorption and fluorescence spectroscopy in solvents of different polarities at room temperature (298 K). Solvatochromic correlations were used to estimate the ground-state (μ_g) and excited-state (μ_e) dipole moments. The excited-state dipole moments for the three molecules were found to be larger than the corresponding ground-state dipole moments.

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1. Introduction

The solvent effect on the absorption and fluorescence characteristics of organic compounds has been the subject of interesting investigations [1]. The excitation of a molecule by photon absorption causes a redistribution of charges which induces conformational changes in the excited state. This can result in an increase or decrease of the excited state dipole moment relative to the ground-state. The study of the ground- and excited-state dipole moments of electronically excited molecules provides important information regarding the electronic and geometric structure of the molecule in the short-lived state. Knowledge of the excited-state dipole moment of electronically excited molecules is quite useful for designing new compounds with nonlinear optical properties, for elucidating the nature of the excited-states, and for determining the course of a photochemical transformation. The excited-state dipole moment of fluorescent dye molecules such as those studied in this report also determines the tenability range of their emission energy as a function of the medium polarity.

The presently available methods for the estimation of single excited-state dipole moments are based on the spectral shift caused externally by electrochromism or internally by solvatochromism. Methods such as electric polarisation of fluorescence [2] and electric dichroism [3]

are generally considered to be very accurate; however, their use is limited by the need for sensitive equipment and the studies have so far been restricted to relatively simple molecules. The solvatochromic method is based on the shift of the UV/vis absorption and fluorescence maxima of solvents with different polarities. Koutek [4] has shown that under suitable conditions, the solvatochromic method gives fairly satisfactory results. Using this technique, the solvent dependence of absorption and fluorescence maxima is used to estimate the excited-state dipole moments of different molecules.

Several workers have used different techniques to perform extensive experimental and theoretical studies on ground-state and excited-state dipole moments of a variety of organic fluorescent compounds, such as coumarins [5–8]. In this context β-diketones have received special attention because of their increasing importance in photophysics and photochemistry. These compounds can exist in solution as both keto and enol tautomers. Since the enolic hydrogen is labile, it can be replaced by a metal cation to form a six-membered chelated ring. The β-diketonate complexes thus formed have been the topic of hundreds of papers and reviews, the research being stimulated by the versatility of these compounds as light-converting optical devices [9–13] and chemi-luminescence activators [14,15]. A β-diketone structure can undergo keto–enol tautomerism in solutions. The relative contributions of the keto and enol tautomers depend on several factors such as the solvent characteristics, temperature and ring structure. In general, many of the diketones exist in solution predominantly in the enolic form at room temperature [16]. The enolic form can exist in different *cis* and *trans*
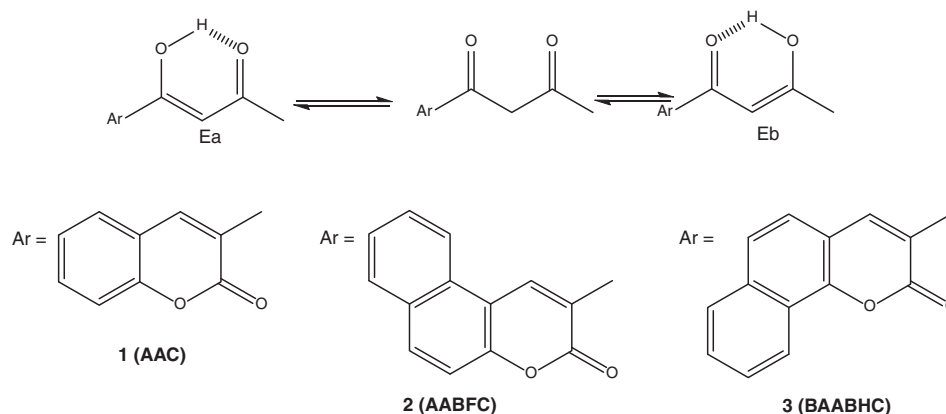
Scheme 1. Keto and enol tautomers.

isomeric forms depending on the temperature, polarity or hydrogen bonding nature of the solvents [17–20].

In the present study we report the estimation of the ground- and excited-state dipole moments of three coumarins [**1** (1-(2-oxo-2*H*-chromen-3-yl)butane-1,3-dione), **2** (1-(3-oxo-3*H*-benzo[*f*]chromen-2-yl)butane-1,3-dione) and **3** (1-(2-oxo-2*H*-benzo[*h*]chromen-3-yl)butane-1,3-dione **3**)] recently synthesised under microwave irradiation [19]. The reaction takes place with excellent yields, short reaction times (<5–10 min) meaning less energy is consumed for heating and in environmentally friendly conditions, that is, less solvent and less added acid (Scheme 1).

We anticipated that the presence and position of the fused benzo ring with the coumarin core could lead to interesting photophysical properties and those compounds could subsequently be used as extraction agents or signalling agents for cation recognition. However, before undertaking complexation studies, the behaviour of the free ligands (**1**, **2** and **3**) was investigated by absorption and fluorescence spectroscopy, single crystal x-ray analysis of **2**, nuclear magnetic resonance (NMR) data and MNDO calculations. The aim of the present study was to estimate the ground-state and excited-state dipole moments and also the change in the dipole moments of dyes **1**–**3** using different methods. This is the first published report for these three dyes.

2. Experimental methods

2.1. Apparatus

All spectrophotometric measurements were conducted at room temperature. UV/vis absorption spectra were recorded on a Varian CARY 50 conc. The estimated experimental error was 2 nm on the band maximum and 5% on the molar extinction coefficient. Fluorescence work was performed on a Varian CARY Eclipse spectrofluorometer. All excitation and emission spectra were corrected. The excitation source was a long life Xenon flash lamp.

2.2. Materials

Coumarin derivatives **1**–**3** were synthesised as reported in the literature [19]. Their molecular structure and purity was confirmed by NMR spectroscopy, mass spectra and x-ray crystal analysis of **2**. The solvents used in the present study, namely acetonitrile, dimethyl sulfoxide, chloroform, ethyl acetate and methanol were of HPLC and spectroscopic grade (purchased from Fluka and Labosi). The required solutions were prepared at a fixed solute concentration (4×10^{-5} M).

2.3. Estimation of the dipole moments

The dipole moment of a molecule in the excited-state is determined by the effect of an electric field (internal or external) on its spectral band position. The solvent dependence of the absorption and fluorescence band maxima is used to estimate the excitation-state dipole moments of different molecules. The equations [Eqs. (1) and (2)] that afford the best results in the change of dipole moments of an excited molecule were suggested by A. Kawski and P. Bojarski [21].

The difference $\overline{\nu}_a - \overline{\nu}_f$:

$$\overline{\nu}_a - \overline{\nu}_f = S_1 f(\varepsilon, n) + const \tag{1}$$

and the sum $\overline{\nu}_a + \overline{\nu}_f$:

$$\overline{\nu}_a + \overline{\nu}_f = -S_2 \Phi(\varepsilon, n) + const \tag{2}$$

where

$$\Phi(\varepsilon, n) = f(\varepsilon, n) + 2g(n) \tag{3}$$

and

$$g(n) = \frac{3}{2} \frac{n^4 - 1}{(n^2 + 2)^2}. \tag{4}$$

In these equations, $\overline{\nu}_a$ and $\overline{\nu}_f$ are the absorption and fluorescence maxima (cm^{-1}), respectively, n and ε are the refractive index and the dielectric constant of solvents, respectively.

The expressions for the solvent parameters $f(\varepsilon, n)$ and $\Phi(\varepsilon, n)$ are given by A. Kawski and Bojarski [21]:

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \tag{5}$$

Table 1
Summary of solvent properties and calculated values of solvent polarity parameters $f(\varepsilon,n)$ and $\Phi(\varepsilon,n)$.

Solvents	μ	ε	n	$f(\varepsilon,n)$	$\Phi(\varepsilon,n)$
Toluene	0.43	2.38	1.4941	0.031	0.698
Chloroform	1.15	4.81	1.443	0.372	0.972
Ethyl acetate	1.88	6.02	1.3723	0.489	0.996
Methanol	1.71	32.7	1.329	0.855	1.302
Acetonitrile	3.45	37.5	1.344	0.863	1.332
DMSO	3.90	46.7	1.4787	0.841	1.488