Quantitative Treatment of the Effect of Solvent on the Electronic Absorption and Fluorescence Spectra of Substituted Coumarins: Evaluation of the First Excited Singlet-State Dipole Moments[1]

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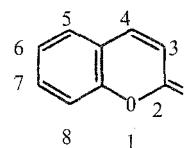
The electronic absorption and fluorescence spectra of coumarin and 11 substituted coumarins were measured in several solvents (dioxane, ethyl ether, ethyl acetate, ethanol, dimethylformamide, acetonitrile, and dimethyl sulfoxide). Ground-state dipole moments were determined in dioxane at 298 K. The results were used to obtain the first excited singlet-state dipole moments of the coumarins under study by the solvatochromic shift method (Bakhshiev, Kawski–Chamma–Viallet, McRae, and Suppan correlations). Also, the ground- and the first excited singlet-state dipole moments were calculated using a combination of the PPP method (π-contribution) and the vector sum of the σ-bond and group moments (σ-contribution). In general, the first excited singlet-state dipole moments of the coumarins are noticeably higher than the corresponding ground-state values, indicating a substantial redistribution of the π-electron densities resulting in a more polar excited state. There is a reasonably good agreement between the calculated and the experimental dipole moments.

INTRODUCTION

As a continuation of our systematic studies of ground- and excited-state dipole moments of biologically important heterocycles;[1-9] we decided to carry out a similar study of coumarin (1) and its derivatives. The

compounds included in this work are coumarin (1), 7-acetoxy-4-methylcoumarin (2), 3-acetylcoumarin (3), 7-amino-4-methylcoumarin (4), 3-coumarincarboxylic acid (5), 7-diethylamino-4-methylcoumarin (6), 4-hydroxycoumarin (7), 7-hydroxycoumarin (8), 7-hydroxy-4-methylcoumarin (9), 7-methoxycoumarin (10), 6-methylcoumarin (11), and 7-methylcoumarin (12). Our previous work on coumarin involved a study of free radical arylation and heteroarylation of coumarin and benzo[*b*]furan, with HMO and SCF-MO calculations used to interpret the results.[10]

1

Coumarin (**1**) is a naturally occurring oxygen-containing heterocycle which can be viewed as a δ-lactone of coumaric (o-hydroxycinnamic) acid. However, its lactonic character is not very pronounced. Coumarin and its derivatives have many different uses, in medicine as anticoagulants[11] and, also, as rodenticides, fluorescent indicators,[12-14] optical brighteners,[15,16] and laser dyes.[17-20]

A number of papers reporting the electronic absorption spectra of coumarins are available.[21-25] While coumarin itself does not fluoresce, substituted coumarins are often fluorescent. Pill-Soon Song and Gordon studied low-temperature fluorescence and phosphorescence of coumarin as well as their respective lifetimes and they compared the experimental data with the results of quantum-chemical calculations (PPP method).[26] Yakatan and co-workers[27,28] and Fink and Köhler[29] studied the singlet excited-state protolytic equilibria of coumarin and several of its hydroxy and methoxy derivatives by fluorescence intensity measurements. The biprotonic phototautomerism kinetics of 7-hydroxy-4-methylcoumarin in its first excited singlet state was investigated by Schulman and Rosenberg.[30] There are several reports in the literature on the effect of pH upon the fluorescence and absorption spectra of 7-hydroxycoumarin derivatives[31-33] and 3-hydroxycoumarin derivatives.[34]

While the dipole moment of coumarin (**1**) has been reported by several groups of authors[35-44] and a study of dipole moments of a series of 7-aminocoumarins has been published,[44] no systematic studies of dipole moments of coumarins seem to be available. Giri and co-workers estimated changes of the dipole moment of several 7-substituted coumarins upon excitation, using the solvatochromic shift method,[45,46] and Baumann and Nagy evaluated the excited-state dipole moments of four coumarins, by means of electrooptical absorption and fluorescence measurements.[47] Also, Pill-Soon Song and Gordon[26] reported the calculated ground-state, first excited singlet-state, and first excited triplet-state dipole moments of coumarin, Sheng and El-Sayed[48] determined its experimental first excited triplet-state value, and McCarthy and Blanchard[49] presented the Austin Model 1 (AM1) semiempirical calculations of the ground-state, first excited singlet-state, and first excited triplet-state dipole moments of several coumarin derivatives.

The goal of the present work is to study the effect of selected solvents (dioxane, ethyl ether, ethyl acetate, ethanol, dimethylformamide, acetonitrile, and dimethyl sulfoxide) upon the electronic absorption and fluorescence (excitation, emission) spectra of coumarin (**1**) and

the substituted coumarins (**2–12**), to measure their ground-state dipole moments, and to determine their first excited singlet-state dipole moments using the solvatochromic shift method (the Bakhshiev and Kawski–Chamma–Viallet equations). Furthermore, we decided to calculate the respective ground- and excited-state dipole moments using a combination of the PPP method (π-contribution) and the σ-bond moments (σ-contribution) and to compare the theoretical and experimental values. The results obtained in this paper should be especially valuable for applications to the use of coumarins as laser dyes and as probes for the polarity of the environment.

EXPERIMENTAL

Chemicals

Coumarin and all coumarin derivatives were obtained from Aldrich Chemical Company, Milwaukee, WI. Analytical-grade solvents were employed to prepare the solutions used in spectroscopic measurements and in the determination of dipole moments.

Instrumentation

Electronic absorption spectra of the coumarins were measured at 296 K in different solvents on a Cary 210 (Varian) spectrophotometer. Fluorescence spectra were recorded at the same temperature on a Perkin–Elmer LS-5 spectrofluorometer.

Experimental Ground-State Dipole Moments

The ground-state dipole moments of coumarins were measured in dioxane at 298 K on a DM-01 dipole meter (Wissenschaftlisch-Technische Werkstätten, Weilheim, Germany) equipped with a DFL-2 cell. Six solvents were used to calibrate the instrument. The refraction indices were obtained with an Abbé refractometer (Bausch & Lomb, Rochester, NY). The dipole moments (μ_g) were evaluated according to the formula[50-53]

$$\mu_g^2 = \frac{27kT}{4\pi N} \cdot \frac{1}{d(D + 2)^2} \cdot (A_D - A_n) \cdot M \qquad (1)$$

where k is the Boltzmann constant (1.381×10^{-16} erg deg^{-1}), T is the absolute temperature, N is Avogadro's number (6.023×10^{23} mol^{-1}), d and D are the density and the dielectric constant of the solvent, respectively,

Table I. Solvent Functions

Solvent	$F_1{}^a$	$F_2{}^b$	$F_3{}^c$	$F_4{}^d$
Dioxane	0.0501	0.3114	0.5882	0.4545
Ethyl ether	0.3762	0.4282	1.0536	0.6901
Ethyl acetate	0.4902	0.4969	1.2519	0.7699
Ethanol	0.8117	0.6516	1.7719	0.9395
Dimethylformamide	0.8356	0.7098	1.8450	0.9597
Acetonitrile	0.8630	0.6659	1.8481	0.9605
Dimethylsulfoxide	0.8377	0.7424	1.8723	0.9670

^{a}Bakhshiev solvent function.
^{b}Kawski–Chamma–Viallet solvent function.
^{c}McRae solvent function.
^{d}Suppan solvent function.

A_D and A_n are the numerical values obtained from the solute dielectric constant and refractive index measurements, respectively, and M is the molecular weight of the solute.

Experimental First Excited Singlet-State Dipole Moments

The excited singlet-state dipole moments were determined by the solvatochromic method. Because some coumarins were fluorescent and some were not, or they displayed only a very weak fluorescence in solvents used in this work, several formulas had to be employed for the treatment of solvent spectrochemical shifts, depending on the respective compounds.

For fluorescent coumarins, the formulas developed by Bakhshiev[54] and Kawski–Chamma–Viallet[55] were used.

Bakhshiev's Formula

$$\tilde{v}_A - \tilde{v}_F = \frac{2(\vec{\mu}_e - \vec{\mu}_g)^2}{a_0^3 hc} \underbrace{\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]\frac{(2n^2+1)}{(n^2+2)}}_{F_2} \quad (2)$$

where v_A and v_F are the absorption and emission maximum wavenumber (cm^{-1}), respectively; μ_g is the permanent dipole moment in the ground state; μ_e is the permanent dipole moment in the first excited singlet state; a_0 is the Onsager cavity radius; D is the solvent dielectric constant; and n is the solvent refractive index.

Kawski–Chamma–Viallet Formula

$$\frac{\tilde{v}_A + \tilde{v}_F}{2} = \frac{2(\mu_e^2 - \mu_g^2)}{a_0^3 hc}$$

$$\underbrace{\left[\frac{2n^2+1}{2(n^2+2)} \cdot \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) + \frac{3(n^4-1)}{2(n^2+2)^2}\right]}_{F_2} \quad (3)$$

where the meaning of the symbols is the same as in formula (2).

For nonfluorescent coumarins two additional formulas, developed by McRae[56] and Suppan,[57] were employed.

McRae's Formula

$$\tilde{v}_A = -\frac{\mu_g(\mu_e - \mu_g)}{a_0^3 hc} \underbrace{\left[\frac{2(D-1)}{D+2}\right]}_{F_3} \quad (4)$$

Suppan's Formula

$$\tilde{v}_A = -\frac{\mu_g(\mu_e - \mu_g)}{a_0^3 hc} \underbrace{\left[\frac{2(D-1)}{2D+1}\right]}_{F_4} \quad (5)$$

The meaning of the symbols in Eqs. (4) and (5) is the same as in Eq. (2). The solvent functions (F_1, F_2, F_3, and F_4) are given in Table I.

The values of the solute cavity radii (a_0) were calculated from the molecular volume of the coumarins according to the equation[58]

$$a_0 = (3M/4\pi\delta N)^{1/3} \quad (6)$$

where M is the molecular weight of the solute, δ is the density of the solute molecule, and N is Avogadro's number. The solid-state densities of the coumarins were determined pycnometrically (25-ml pycnometer) at 298 K in the form of a suspension of the respective compound (130 to 440 mg) in kerosene (d_4^{25}, 0.7753). The results are shown in Table II.

Theoretical Ground- and Excited-State Dipole Moments

A combination of the PPP (Pariser–Parr–Pople, π–LCI–SCF–MO) method[59,60] and the empirical σ–bond moment contributions was used to obtain the total dipole

Table II. Solid-State Densities (d^{25}_4) and Solute Cavity Radii (a_o) of Coumarins

No.	Substituent(s)	MW	d^{25a}_4	a_o (Å)[b]
1	—	146.15	1.478	3.40
2	7-Acetoxy-4-methyl	218.21	1.339	4.01
3	3-Acetyl	188.18	1.492	3.68
4	7-Amino-4-methyl	175.19	1.215[c]	3.85[d]
5	3-Carboxylic acid	190.15	1.764[d]	3.50[d]
6	7-Diethylamino-4-methyl	231.30	1.215	4.23
7	4-Hydroxy	162.14	1.293	3.68
8	7-Hydroxy	162.14	1.591	3.96
9	7-Hydroxy-4-methyl	176.17	1.351	3.73
10	7-Methoxy	176.17	1.268	3.80
11	6-Methyl	160.17	1.264	3.69
12	7-Methyl	160.17	1.346	3.99

[a]See the text.
[b]Calculated according to Suppan's Eq. (6)[58] (see the text).
[c]Estimated value.
[d]Approximate value.

Table III. Parameters Used in the PPP Calculations[a]

Atom, r[b]	I_r	A_r	γ_{rr}	n_r	β_{c-r}	β_{c-r}/B_{c-c}	ℓ_{c-r}
C	11.22	0.69	10.53	1	−2.318	1.000	1.40
O$_{(endo)}$	27.17	12.59	14.58	2	−2.550	1.100	1.40
O$_{(c=0)}$	16.10	2.10	14.00	1	−2.225	0.960	1.23
O(OH)	32.90	10.00	22.90	2	−2.318	1.000	1.40
O(OMe)	33.80	10.80	23.00	2	−2.040	0.880	1.40
CO.Me (Ac)	16.54	2.27	14.27	2	−1.958	0.845	1.40
NH$_2$	27.30	9.30	18.00	2	−1.854	0.800	1.40
NEt$_2$	28.70	10.70	18.00	2	−1.640	0.708	1.40
Me[c]	24.79	13.12	11.67	2	−1.377	0.594	1.52

[a]Values in eV. I_r and A_r are valence-state ionization energies and electron affinities, respectively. The one-center electronic repulsion integrals and the core resonance integrals between the nearest neighbors are represented by γ_{rr} and β_{c-r}, respectively; n_r is the number of electrons contributed to the π-system by atom r; and ℓ_{c-r} is the covalent bond between atom C and atom r (Å). Most of the parameters are those used in our previous work[7].
[b]COOH and COOMe were treated as a 4π-electron group with 3π-electron centers, with the individual parameters for C, O (C=O), OH, and OMe as shown.
[c]Heteroatom model.

moments, μ_t, as a vector sum of the respective π- and σ-contributions, μ_π and μ_σ. The calculations were carried out on a Hewlett–Packard HP 150 II Touchscreen computer with a 8087 coprocessor using the parameters shown in Table III.

To obtain the π-contribution, μ_π, interactions between monoexcited configurations formed by promotion of one electron from one of the four highest occupied MOs to one of the four lowest unoccupied MOs were considered. The six-membered rings were assumed to be

Table IV. Bond and Group Moments (D) Used for Calculations of σ-Contributions to the Total Dipole Moments[a]

$\overset{+}{r}\overset{-}{-s}$	μ_G	$\overset{+}{r}\overset{-}{-s}$	μ_G
H–C	0.63	H–O	1.53
Me–C	0.37	H$_2$N–C	1.53[b]
C–O	0.86	Et$_2$N–C	1.58[c]
C=O	0.86		

[a]For a detailed explanation of the choice of the values, see Refs. 62–65.
[b]For ϕ = 48.5°; ϕ is the angle between the r–s bond and the direction of the group moment.
[c]For ϕ = 30°.

planar and to possess idealized geometry (regular hexagons). SCF MOs served as the basis for CI calculations and only resonance integrals between nearest neighbors were considered.

The Mataga–Nishimoto formula[61] was used for the bicentric repulsion integrals:

$$\gamma_{\mu\nu} = \frac{14.399}{\ell_{\mu\nu} + 1.328} \, eV$$

where $\ell_{\mu\nu}$ (Å) is the distance between atom μ and atom ν.

The σ-contributions, μ_σ, to the total dipole moments have been calculated using bond dipole moments and group dipole moments.[62–65] The bond and group moments used in our calculations are similar to those employed in the case of pyrimidines[7] and are reported in Table IV.

The excited singlet-state dipole moments were computed using a combination of the PPP method and the empirical σ-bond contributions. In the case of the π-contribution, it was assumed that the 1-1' (HOMO → LUMO) π → π* transition was most important, while the σ-contribution was assumed to remain the same in the excited state as it was in the ground state.

RESULTS AND DISCUSSION

Solvent Effects on the Absorption and Fluorescence Spectra

The electronic absorption and fluorescence excitation and emission spectra of the above-mentioned coumarin derivatives were investigated in several solvents of different polarities.

The spectral absorption properties are summarized in Table V. It can be seen that most of the coumarins under study are characterized by the presence of three

Table V. Absorption Spectral Characteristics of Coumarins in Various Solvents[a]

Comp. No.	Substituent(s)	Solvent[b]	λ (nm) (logε)[c]						
1	None	Dioxane	270	(4.300),	*280, 309*	(3.995)			
		Ethyl ether	271	(4.299),	*280, 309*	(3.974)			
		Ethyl acetate	272	(4.302),	*280, 309*	(4.004)			
		Ethanol	273	(4.203),	*280, 309*	(3.905)			
		Dimethylformamide	274	(4.344),	*280, 309*	(4.043)			
		Acetonitrile	271	(4.326),	280, 309	(4.008)			
		Dimethylsulfoxide	274	(4.315),	280, 309	(4.015)			
2	7-Acetoxy-4-methyl	Dioxane	217	(5.220),	271	(5.011),	*276, 308*	(4.940),	*312*
		Ethyl ether	270	(4.981),	*308*	(4.868)			
		Ethyl acetate	247	(4.743),	270	(5.050),	*308*	(4.987)	
		Ethanol	206	(5.283),	273	(4.922),	*275*	(4.877)	
		Dimethylformamide	273	(4.994),	*278, 308*	(4.938),	*313*		
		Acetonitrile	270	(5.060),	275, 308	(4.999)	*315*		
		Dimethylsulfoxide	253	(4.769),	·275	(4.947),	*278, 308*	(4.907),	312
3	3-Acetyl	Dioxane	299	(3.994),	337	(3.857)			
		Ethyl ether	297	(3.939),	337	(3.805)			
		Ethyl acetate	296	(3.975),	337	(3.767)			
		Ethanol	298	(4.092),	337	(3.899)			
		Dimethylformamide	300	(3.959),	338	(3.822)			
		Acetonitrile	208	(4.335),	298	(4.143),	338	(3.938)	
		Dimethylsulfoxide	301	(4.000),	338	(3.848)			
4	7-Amino-4-methyl	Dioxane	214	(4.371),	228	(4.210),	340	(4.374)	
		Ethyl ether	213	(4.821),	339	(4.383)			
		Ethyl acetate	340	(4.328)					
		Ethanol	205	(4.677),	230	(4.301),	350	(4.354)	
		Dimethylformamide	349	(4.458)					
		Acetonitrile	205	(4.656),	228	(4.227),	342	(4.348)	
		Dimethylsulfoxide	258	(3.756),	356	(4.477)			
5	3-Carboxylic	Dioxane	216	(4.261),	294	(4.198),	332	(3.991)	
		Ethyl ether	209	(4.263),	294	(4.061),	330	(3.852)	
		Ethyl acetate	296	(4.160)					
		Ethanol	203	(4.475),	292	(4.211)			
		Dimethylformamide	290	(4.260)					
		Acetonitrile	201	(4.520),	299	(4.179)			
		Dimethylsulfoxide	291	(4.267)					
6	7-Diethylamino-4-methyl	Dioxane	215	(4.036),	239	(3.812),	361	(4.108)	
		Ethyl ether	209	(4.321),	237	(3.915),	353	(4.206)	
		Ethyl acetate	251	(3.747),	361	(4.137)			
		Ethanol	209	(4.262),	242	(3.889),	372	(4.123)	
		Dimethylformamide	370	(4.248)					
		Acetonitrile	208	(4.342),	239	(3.965),	368	(4.194)	
		Dimethylsulfoxide	259	(3.888),	375	(4.373)			
7	4-Hydroxy	Dioxane	216	(4.295),	276	(4.002),	279	(4.002),	*290, 314*
		Ethyl ether	213	(4.301),	266	(3.969),	277	(3.970),	*290, 314*
		Ethyl acetate	266	(4.268),	278	(4.262),	*290, 306*	(4.130),	*314*
		Ethanol	266	(4.330),	278	(4.298),	*290, 306*	(4.147),	*314*
		Dimethylformamide	268	(4.089),	300	(4.105),	*290, 306*	(3.986),	*314*
		Acetonitrile	268	(4.270),	280	(4.274),	*290, 306*	(4.088),	*314*
		Dimethylsulfoxide	267	(4.259),	288	(4.261),	*290, 306*	(4.113),	*314*
8	7-Hydroxy	Dioxane	320	(4.255)					
		Ethyl ether	*296, 315*	(4.143)					
		Ethyl acetate	*290, 317*	(4.176)					
		Ethanol	*306, 326*	(4.155)					
		Dimethylformamide	*290, 309,* 323	(4.152)					
		Acetonitrile	*290, 310,* 319	(4.018)					
		Dimethylsulfoxide	*290, 300,* 325	(4.179)					

Table V. Continued

Comp. No.	Substituent(s)	Solvent[b]		λ (nm) (logε)[c]				
9	7-Hydroxy-4-methyl	Dioxane	223	(4.775),	*290, 310,*		318	(4.091)
		Ethyl ether	208	(4.351)	*290, 310,*		319	(4.151)
		Ethyl acetate	*290, 310,* 319	(4.151)				
		Ethanol	*290, 310,* 324	(4.227)				
		Dimethylformamide	243	(2.778),	*290, 310,*		321	(4.053)
		Acetonitrile	215	(4.268),	*290, 309,*		317	(4.170)
		Dimethylsulfoxide	*290, 310,* 322	(4.543)				
10	7-Methoxy	Dioxane	216	(4.200),	*296, 302,*		319	(4.180)
		Ethyl ether	319	(4.201),	*309*			
		Ethyl acetate	319	(4.151),	*309*			
		Ethanol	205	(4.340),	216	(4.228),	322	(4.255)
		Dimethylformamide	320	(4.332),	*209, 309*			
		Acetonitrile	319	(4.158),	*209, 309*			
		Dimethylsulfoxide	320	(4.320)				
11	6-Methyl	Dioxane	250	(3.910),	275	(4.012),	322	(3.679)
		Ethyl ether	217	(3.273),	273	(3.013),	320	(2.626)
		Ethyl acetate	247	(3.863),	273	(4.212),	321	(3.834)
		Ethanol	205	(4.324),	276	(4.082),	321	(3.723)
		Dimethylformamide	276	(4.328),	322	(3.959)		
		Acetonitrile	247	(3.880),	273	(4.226),	320	(3.851)
		Dimethylsulfoxide	253	(3.951),	278	(4.277),	323	(3.930)
12	7-Methyl	Dioxane	214	(4.905),	278	(4.041),	*285,* 314	(4.594)
		Ethyl ether	213	(4.283),	277	(4.112),	*285,* 309	(3.930)
		Ethyl acetate	277	(4.009),	312	(3.849)		
		Ethanol	212	(4.472),	285	(4.277),	312	(4.144)
		Dimethylformamide	286	(4.077),	314	(3.946)		
		Acetonitrile	213	(4.112),	283	(3.966),	313	(3.831)
		Dimethylsulfoxide	287	(3.969),	314	(3.855)		

[a]The concentrations of coumarins were between $2 \cdot 10^{-5}$ and 10^{-4} M.

[b]Solvents are listed in order of increasing dielectric constant value.

[c]Absorption maxima. Wavelength precision, ± 1 nm. Italic wavelength values correspond to the shoulders. The logarithm of the molar absorption coefficient (M^{-1} cm^{-1}) is given in parentheses.

main absorption bands, in the regions of 200–220, 260–290, and 310–370 nm. The shortest-wavelength bands, which generally have the highest molar absorption coefficient values (logε = 4.3–5.2), can be attributed to π→π* [1]B transitions, whereas the long-wavelength bands, with weaker, but quite high molar absorption coefficients (logε = 2.8–4.8), belong to the π → π* [1]L$_a$ and [1]L$_b$ transitions. As noted previously, the lowest π→π* ([1]L$_b$) transition of coumarins is polarized practically along the long molecule axis and is localized mainly in the 1,2-pyrone ring.[26] No n→π* transitions were observed. Nevertheless, the presence of shoulders for some of the considered 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 group in the pyrone moiety. Only slight red shifts of the absorption band maxima (Δλ$_a$ = 1 to 16-nm) of the coumarin derivatives were observed when increasing the polarity of the solvent.

Five of the twelve studied coumarin derivatives exhibited no fluorescence: coumarin 1, 7-acetoxy-4-methyl-coumarin 2, 3-acetylcoumarin 3, 6-methylcoumarin 11, and 7-methylcoumarin 12. It is already known that coumarin exhibits no fluorescence, although a weak emission at 77 K has been reported.[26]

For the rest of the compounds the excitation and emission fluorescence characteristics are reported in Table VI. The fluorescence excitation spectra contain bands generally situated at a wavelength close to those of the absorption spectra.

The emission spectra of coumarins include only one band, in the 370- to 440-nm region, depending on the compound. The fact that most compounds exhibited a marked red shift of the fluorescence emission spectra upon increasing the solvent polarity is further evidence of a π* → π transition (Fig. 1).

A peculiar behavior is exhibited by 7-methoxycoumarin: it is the intensity and not the wavelength of the

Table VI. Fluorescence Excitation and Emission Spectral Properties of Coumarins in Various Solvents[a]

Comp. No.	Substituent(s)	Solvent[b]	λ_{ex} (nm)[c]	λ_{em} (nm)[d]
4	7-NH₂-4-Me	Dioxane	341	404
		Ethyl ether	340, *350*	394
		Ethyl acetate	342	400
		Ethanol	351	427
		Dimethyl-formamide	349	416
		Acetonitrile	342	412
		Dimethyl-sulfoxide	352	421
5	3-COOH	Dioxane	308	405
		Ethyl ether	301, 335	400
		Ethyl acetate	300, 334	404
		Ethanol	303, 337	414
		Dimethyl-formamide	302, 336	408
		Acetonitrile	300, 337	410
		Dimethyl-sulfoxide	304, 339	420
6	7-NEt₂-4-Me	Dioxane	358	415
		Ethyl ether	356	404
		Ethyl acetate	358	417
		Ethanol	384, *362*	443
		Dimethyl-formamide	381, *362*	432
		Acetonitrile	362, *373*	432
		Dimethyl-sulfoxide	386, *375*	436
7	4-OH	Dioxane	290, *325*	369
		Ethyl ether	291, *322*	374
		Ethyl acetate	291, *323*	376
		Ethanol	289, *320*	370
		Dimethyl-formamide	296, *328*	381
		Acetonitrile	296, *328*	390
		Dimethyl-sulfoxide	300, *327*	395
8	7-OH	Dioxane	328, *332*	380
		Ethyl ether	328, *333*	385
		Ethyl acetate	329, *331*	380
		Ethanol	330, *334*	386
		Dimethyl-formamide	331, *333*	389
		Acetonitrile	327, *332*	390
		Dimethyl-sulfoxide	329, *332*	397
9	7-OH-4-Me	Dioxane	323, *293, 330*	375
		Ethyl ether	324, *290*	374
		Ethyl acetate	321, *292*	372
		Ethanol	323, *293, 331*	382
		Dimethyl-formamide	325, *294*	382
		Acetonitrile	320, *292*	377
		Dimethyl-sulfoxide	326, *293*	384

Table VI. Continued

Comp. No.	Substituent(s)	Solvent[b]	λ_{ex} (nm)[c]	λ_{em} (nm)[d]
10	7-MeO	Dioxane	327	382
		Ethyl ether	326	379
		Ethyl acetate	326	381
		Ethanol	326	382
		Dimethyl-formamide	331	385
		Acetonitrile	326	381
		Dimethyl-sulfoxide	329	386

[a]The concentrations of the coumarins were between 10^{-6} and 10^{-5} M.
[b]Solvents are listed in order of increasing dielectric constant.
[c]Excitation maxima. Wavelength precision, ±1 nm. Italic wavelength values correspond to shoulders.
[d]Emission maxima. Wavelength precision, ±1 nm. Italic wavelength values correspond to shoulders.
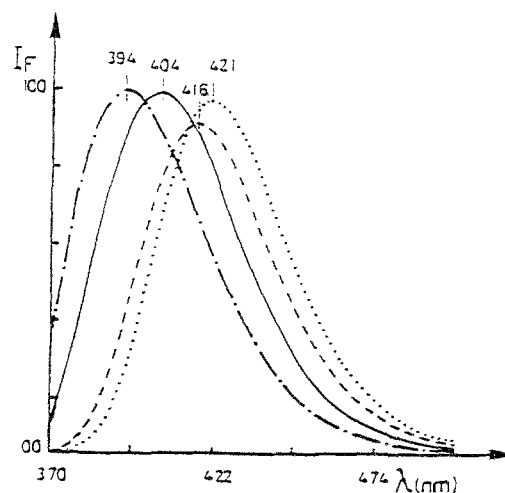

Fig. 1 Effect of the polarity of the solvent upon the fluorescence emission spectra of 7-amino-4-methylcoumarin. Solvents: dimethylformamide (- - -); dimethylsulfoxide (·····); dioxane (——); ethyl ether (.-.-.).

emission maxima that changes significantly with the solvent polarity, the variation of the fluorescence intensity with the solvent dielectric constant being practically linear. In a previous work Wenska and Paszyc[66] also reported an increasing in the quantum yield with the solvent polarity for 7-methoxycoumarin. They attributed this variation to the fact that in a nonpolar solvent the $^1n\pi^*$ and $^3n\pi^*$ states are positioned, respectively, higher and lower than the $\pi\pi^*$ singlet state, thus facilitating intersystem crossing, whereas in polar solvents the position of the $\pi\pi^*$ singlet state is lower than that of the $^3n\pi^*$ state. Consequently, intersystem crossing dimin-

ishes and the fluorescence quantum yield increases in polar solvents.

Experimental and Calculated Ground-State Dipole Moments

In Table VII, we have compared the calculated and experimental ground-state dipole moments of the coumarins under study. The direction of the calculated dipole moments is shown as well. There is generally a good agreement between the experimental and the theoretical values. Indeed the differences between both sets of values range from about 1.2 to 34%. These differences are comparable to those previously reported in a similar study on phenothiazines.[9]

Excited Singlet-State Dipole Moments

To evaluate the excited singlet-state dipole moments of the coumarin derivatives, we first plotted the Stokes shifts $(\bar{\nu}_A - \bar{\nu}_F)$ and $(\bar{\nu}_A + \bar{\nu}_F)/2$ against the solvent functions F_1 and F_2 for the fluorescent compounds and of $\bar{\nu}_A$ against the solvent functions F_3 and F_4 for the nonfluorescent ones according to Eqs. (2) and (3) and Eqs. (4) and (5), respectively. The values of the solvent functions are shown in Table I.

We used the wavenumbers corresponding to the ^1L_a (or ^1L_b) maxima situated in the 260- to 380-nm region and the wavenumbers corresponding to the fluorescence maxima.

The results of the statistical treatment of the Bakhshiev, Kawski–Chamma–Viallet, MacRae, and Suppan correlations, i.e., the slopes, intercepts, and correlation coefficients are presented in Table VIII (Figs. 2 and 3). The correlation coefficients for the fluorescent compounds are larger than 0.92, which indicates a satisfactory linearity for all correlations. Nevertheless, the Kawski–Chamma–Viallet correlation fits a larger number of solvents than the Bakhshiev correlation. The MacRae and Suppan correlations present comparable results except for 3-acetylcoumarin and 4-hydroxycoumarin (unsatisfactory correlation). Several solvents, i.e., dioxane, acetonitrile, and ethanol, systematically exhibited deviations from linearity and were therefore excluded from the correlations. This may be due to the specific solute–solvent interactions (hydrogen bonds) and, also, to the assumptions made in the solvatochromic method itself.

The first excited singlet-state dipole moments determined from the slopes of the Bakhshiev, Kawski–Chamma–Viallet, MacRae, and Suppan correlations are

Table VII. Comparison of Calculated and Experimental Ground-State Dipole Moments of Coumarins[a]

No.	Substituent(s)	$\vec{\mu}_{G\text{calc}}$[b]	θ[c]	$\mu_{G\text{exp}}$[d]
1	—	5.15[e]	−14°	4.77[f]
2	7-Acetoxy-4-methyl	5.76	−67°	4.86
3	3-Acetyl	6.98	5°	4.55
4	7-Amino-4-methyl	7.07	−12°	6.33
5	3-Carboxylic acid	7.10	19°	5.70
6	7-Diethylamino-4-methyl	6.86	−16°	6.78
7	4-Hydroxy	5.96	−44°	5.00
8	7-Hydroxy[g]	5.75	−16°	4.94
9	7-Hydroxy-4-methyl	5.93	−18°	5.20
10	7-Methoxy	5.27	−21°	4.89
11	6-Methyl	6.12	−32°	5.05
12	7-Methyl	6.13	−31°	4.79

[a]All values as D.
[b]Calculated ground-state dipole moment.
[c]Calculated angle between the positive direction of the x axis and the direction of the total calculated dipole moment read counterclockwise; for this orientation,
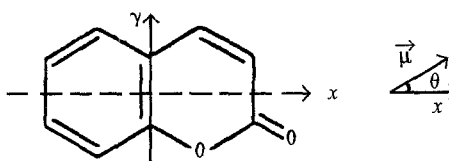
[d]Experimental ground-state dipole moment, in dioxane (298 K).
[e]Examples of calculated values in the literature[26]: PPP, 4.07 and 5.18 D; CNDO/2, 4.62 D.
[f]Literature gives 4.61 D in dioxane[42]: for other values see Refs. 35–41, 43, and 44.
[g]Umbelliferone.

given in Table IX. For most coumarins a rather satisfactory agreement is observed between the excited singlet-state dipole moments obtained from these correlations. These dipole moment values are compared with the experimental ground-state values. The dipole moments of all the compounds under study are higher in the first excited state than in the ground state. The difference is approximately 0.6 to 3 D for the Bakhshiev and Kawski–Chamma–Viallet correlations and significantly larger for the MacRae and Suppan correlations. The fact that the first excited singlet state of 7-amino- and 7-diethylamino-4-methylcoumarin displays a much larger dipole moment than the ground state may be attributed to an intense resonance electron-donating effect of the amino and diethylamino substituents in the excited singlet state of these compounds, the interactions between the π system and the chromophore NH_2 or NEt_2 present in the 7-position leading to a strong electronic delocal-

Table VIII. Statistical Treatment of the Correlations of the Spectral Shifts of Coumarin Derivatives

Comp. No.	Substituent(s)	Slope	Intercept	Correlation coefficient	No. of data
	Bakhshiev correlation				
4	7-Amino-4-methyl	1,948	3,424	0.960	4
5	3-Carboxylic acid	3,413	7,562	0.965	5
6	7-Diethylamino-4-methyl	345	3,576	0.987	3
7	4-Hydroxy	1,607	8,672	0.990	4
8	7-Hydroxy	840	4,867	0.994	4
9	7-Hydroxy-4-methyl	1,055	4,099	0.930	5
10	7-Methoxy	942	4,622	0.990	4
	Kawski–Chamma–Viallet correlation				
4	7-Amino-4-methyl	−4,275	29,336	0.955	5
5	3-Carboxylic acid	−1,246	30,038	0.980	4
6	7-Diethylamino-4-methyl	−5,227	28,578	0.932	6
7	4-Hydroxy	−4,964	33,659	0.94	5
8	7-Hydroxy	−3,371	30,621	0.915	5
9	7-Hydroxy-4-methyl	−1,301	29,507	0.932	5
10	7-Methoxy	−855	29,226	0.974	5
	McRae correlation				
1	None	−415	37,301	0.983	6
2	7-Acetoxy-4-methyl	−169	3,826	0.970	4
3	3-Acetyl			NC[a]	
4	7-Amino-4-methyl	−1,484	31,124	0.958	5
5	3-Carboxylic acid	−453	34,359	0.940	5
6	7-Diethylamino-4-methyl	−1,619	29,899	0.947	6
7	4-Hydroxy			NC	
8	7-Hydroxy	−964	32,659	0.969	4
9	7-Hydroxy-4-methyl	−332	31,682	0.903	6
10	7-Methoxy	−138	31,505	0.984	5
11	6-Methyl	−577	37,285	0.975	4
12	7-Methyl	−1,540	37,845	0.961	6
	Suppan correlation				
1	None	−1,054	37,560	0.969	6
2	7-Acetoxy-4-methyl	−72	3,787	0.933	5
3	3-Acetyl			NC	
4	7-Amino-4-methyl	−4,402	32,619	0.953	5
5	3-Carboxylic acid	−1,117	34,612	0.914	5
6	7-Diethylamino-4-methyl	−4,872	31,589	0.948	6
7	4-Hydroxy			NC	

Table VIII. Continued

Comp. No.	Substituent(s)	Slope	Intercept	Correlation coefficient	No. of data
8	7-Hydroxy	−3,007	33,767	0.972	4
9	7-Hydroxy-4-methyl	−699	31,807	0.923	5
10	7-Methoxy	−410	31,644	0.971	5
11	6-Methyl	−2,079	38,137	0.923	5
12	7-Methyl	−4,535	39,381	0.959	6

[a]No correlation.
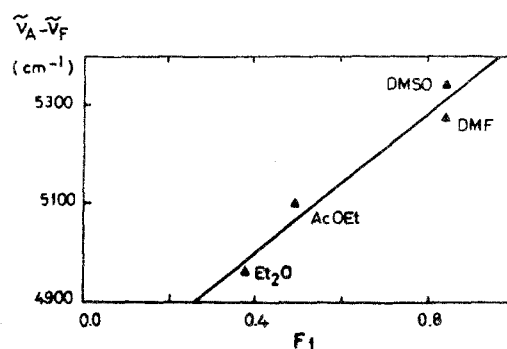
Fig. 2 Bakhshiev's correlation between the solvent spectral shift and the solvent function F_1 for 7-methoxycoumarin.
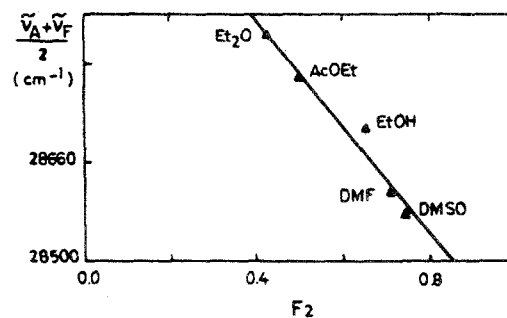
Fig. 3 Kawski–Chamma–Viallet correlation between the solvent spectral shift and the solvent function F_2 for 7-methoxycoumarin.

ization and, thus, giving a high value of the dipole moment.

A redistribution of the electric charges is supposed to occur upon excitation of the molecules, leading to a substantially different distribution of the electronic charge in the excited state. The lowest $\pi^* \rightarrow \pi$ transition is polarized along the long molecular axis and is localized mainly in the pyrone ring.[26]

Table IX. Ground and Singlet Excited-State Dipole Moments of Coumarins[a]

Comp. No.	Substituent(s)	μG[b]	$\mu S1$[c]	$\mu S1$[d]			
				I[e]	II[f]	III[g]	IV[h]
1	None	4.77	2.67[i]	NF[j]	NF	6.50	5.45
2	7-Acetoxy-4-methyl	4.86	3.38	NF	NF	5.05	5.31
3	3-Acetyl	4.55	8.06	NF	NF	NC[k]	NC
4	7-Amino-4-methyl	6.33	7.63[l]	9.65	8.02	8.99	14.22
5	3-Carboxylic acid	5.70	5.79	9.51	6.15	6.38	7.37
6	7-Diethylamino-4-methyl	6.78	5.15	8.39	9.23	10.37	17.60
7	4-Hydroxy	5.00	2.75	7.82	7.04	NC	NC
8	7-Hydroxy	4.94	5.85	7.22	6.72	7.35	12.43
9	7-Hydroxy-4-methyl	5.20	5.12[m]	7.53	5.81	5.86	6.59
10	7-Methoxy	4.89	4.43	7.16	5.36	5.20	5.81
11	6-Methyl	5.05	3.65	NF	NF	9.16	6.19
12	7-Methyl	4.79	3.30	NF	NF	16.75	8.85

[a] In D.

[b] Experimental ground-state dipole moments.

[c] Calculated by the PPP method for first-excited singlet-state dipole moments.

[d] Experimental first-excited singlet-state dipole moment values.

[e] Bakhshiev's correlations.

[f] Kawski–Chamma–Wiallet correlations.

[g] McRae correlations.

[h] Suppan correlations.

[i] Lit. value: 6.21 D[49].

[j] Non-fluorescent.

[k] No correlation.

[l] Lit. value: 8.19 D[49].

[m] Lit. value: 5.32 D[49].

The PPP calculations of the first excited singlet-state dipole moments predict a decrease in polarity of the coumarin derivatives **1**, **2**, **6**, **7**, **10**, **11**, and **12**, an increase in polarity for compounds **3**, **4**, and **8**, and almost no variation for compounds **5** and **9**, with respect to the ground-state values (Table IX). Experimental values predict an increase in singlet-state dipole moment for all compounds. The validity of the experimental solvatochromic method is confirmed by the relatively good agreement found between the values predicted by the Kawski–Chamma–Viallet and Suppan correlations for compounds **4**, **5**, **6**, **8**, **9**, and **10**.

Furthermore, our excited singlet-state dipole moment experimental values obtained with the Kawski–Chamma–Viallet correlation for compounds **4** and **9** and with the Suppan correlation for compounds **1**, **4**, and **9** are in good accord with the calculated values reported recently by McCarthy and Blanchard,[49] using the AM1 method.

The difference between the experimental and the calculated excited singlet-state dipole moments of some of the considered coumarins may be due partly to the

various assumptions and simplifications made in the use of the Bakhshiev, Kawski–Chamma–Viallet, McRae, and Suppan correlations[4,7,67] and, also, to the strong specific effects of the solvents of different natures occurring in the excited singlet state. In addition, application of the PPP calculations is subject to uncertainties since the charge distribution of molecules in the excited state is not always completely evaluated.[67]

ACKNOWLEDGMENTS

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