Excited-State Dipole Moment of 7-Aminocoumarins as Determined from Time-Resolved Microwave Dielectric Absorption Measurements

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The excited-state dipole moments of several structurally related 7-aminocoumarin derivatives, used as laser dyes and in nonlinear applications, have been measured directly by following time-resolved changes in photoinduced microwave dielectric absorption. The dipole moments of the systems in the fluorescent state lie between 8.1 and 11.9 D, and the changes in the dipole moment on electronic excitation range between 1.7 and 6.1 D. Further, the excited-state dipole moment of any given system is found to be almost the same in benzene and in 1,4-dioxane. The results unambiguously suggest that these aminocoumarins fluoresce from the locally excited state and not from a zwitterionic or twisted intramolecular charge-transfer state, as often indicated in the literature.

Introduction

The dipole moment of an electronically excited-state molecule is an important property that provides information on the electronic and geometrical structure of the molecule in the short-lived excited state. A knowledge of the excited-state dipole moment of electronically excited molecules is quite useful in designing nonlinear optical materials, elucidating the nature of the excited states, and determining the course of a photochemical transformation. The excited-state dipole moment of fluorescent dye molecules such as those studied here also determines the tunability range of the emission energy as a function of the polarity of the medium.

Whereas the ground state dipole moment of a chemical system can be measured rather accurately, not many reliable techniques are available for the determination of the dipole moment of short-lived species such as electronically excited states of a molecule or photochemical transients such as radicals, etc. Among the existing methods for the determination of the change in dipole moment ($\Delta\mu = \mu_e - \mu_g$) associated with electronic excitation of a molecule, the most popular are based on a linear correlation between the difference in the wavenumbers of the absorption and fluorescence maxima ($\bar{\nu}_a - \bar{\nu}_f$) and a solvent polarity function, which usually involves both the dielectric constant (ϵ) and the refractive index (n) of the medium.[1−3] Although a number of formulations of this linear correlation are known,[3] the expression most commonly used is the one developed by Lippert and Mataga.[1,2] This expression (eq 1) is based on Onsager's reaction-field theory that assumes the fluorophore to be a point dipole held in the center of a spherical cavity (Onsager cavity) in a homogeneous and continuous dielectric. According to the Lippert−Mataga equation, $\Delta\bar{\nu}$ of a fluorophore is related to the solvent polarity function, Δf as follows:

$$\bar{\nu}_a - \bar{\nu}_f = [2(\mu_e - \mu_g)^2\Delta f]/(hca^3) + \text{constant} \qquad (1)$$

$$\text{where } \Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

Hence, $\Delta\mu$ can simply be estimated from the slope of the plot of $\bar{\nu}_a - \bar{\nu}_f$ against Δf.

Although the experimental procedures for the measurement of $\Delta\mu$ appear to be rather simple, one of the major drawbacks of this method is that the $\Delta\mu$ values to be estimated depend critically on the choice of the value of a, the molecular interaction radius (the radius of the spherical Onsager cavity). This quantity is most often chosen rather arbitrarily, which impairs the efficacy of this solvatochromic method, so that the $\Delta\mu$ values obtained by this method cannot be relied upon. Although the uncertainty of the value of the Onsager cavity radius has been partially ameliorated in the modified version of eq 1,[5] which correlates $\Delta\bar{\nu}$ with the microscopic solvent polarity parameter, $E_T(30)$,[4] the equation nevertheless cannot be expected to provide reliable and accurate $\Delta\mu$ values. A thermochromic method that is similar in principle, in which the variation of ϵ and n is brought about by temperature changes, is also used.[6] The effect of external electric fields on the absorption and fluorescence band positions and intensities (electrooptical absorption and emission methods)[7,8] has also been studied to determine the ground- and excited-state dipole moments of a molecule. Braun and co-workers developed methods for the determination of the excited-state dipole moment by measuring photoinduced changes of the amplitudes of the dc photoconductivity signal[9] and also by analyzing the shape of this signal induced by polarized light.[10] Fessenden and co-workers, on the other hand, developed a method for the determination of the dipole moment of transients such as radicals and excited states of molecules from a quantitative measurement of the changes in the microwave dielectric absorption (or loss) following electronic excitation.[11−14] A slightly modified method was subsequently developed[15] and extensively used by Warman and co-workers for the study of the excited states of several interesting electron donor−acceptor systems.[16]

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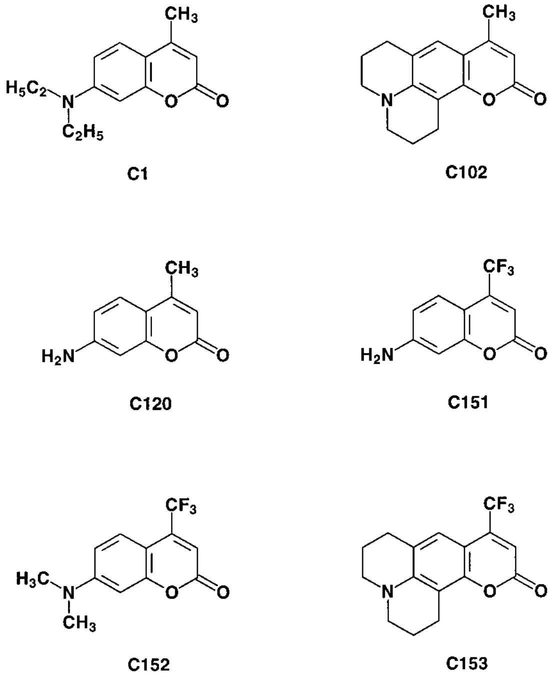
CHART 1



In this paper, time-resolved changes in the microwave dielectric loss behavior of several 7-aminocoumarin derivatives (Chart 1) have been studied with a view to determining their excited-state dipole moments. The 7-aminocoumarins are a family of compounds that have been extensively studied for several reasons.[17−57] They are strongly luminescent and fairly stable systems, ideally suited for application as laser dyes.[17] The solvatochromic absorption and fluorescence behavior of these electron donor−acceptor (EDA) systems suggests an enhanced separation of charge in the excited state.[42] This property has made the aminocoumarins attractive fluorescence probes for the study of solvent reorganization and dynamics[18−29,44−49] and also for the study of various microheterogeneous assemblies.[30−32] These systems, like other EDA molecules, have also been investigated to explore their suitability as nonlinear optical materials.[39] Other issues that have been the focus of several studies are whether the fluorescence of the flexible aminocoumarins originates from a twisted intramolecular charge-transfer (TICT) state and whether there exists a low-lying nonfluorescent TICT state or other electronic state in close proximity to the fluorescent state.[25,40−43,50−54]

What is important to note in this context is that the magnitude of the change in dipole moment on electronic excitation of the aminocoumarins is the most important parameter that determines the nature of the emitting state (locally excited or TICT) and, hence, the extent of solvatochromism and the suitability as a nonlinear optical material or as a fluorescent probe for the study of solvation. Quite obviously, a number of theoretical and experimental studies undertaken on the coumarins are aimed at evaluation of the excited-state dipole moment.[33−41,57] Even though the excited-state dipole moments of these systems have been estimated by several experimental and theoretical methods, the values differ significantly, as each method suffers from one drawback or another. Herein, we report the results of a time-resolved microwave absorption study that is definitely superior to any other methods employed earlier and is one of the most direct methods for the estimation of the excited-state dipole moments.

Experimental Section

Materials. The aminocoumarin derivatives used in this study were procured from Eastman Kodak Company, were of laser grade, and were used without any further purification. The reference compound, diphenylcyclopropenone (DPCP), was obtained from Aldrich and recrystallized from an ethanol−water mixture before the experiments. The solvents were of the best available grade from Aldrich or Fischer Scientific and were used without purification. Argon- bubbled solutions were used for microwave experiments.

Methodology. Measurement of the dipole moment is based on the principle that an addition of a dipolar solute to a nonpolar solvent introduces a dielectric loss that is related to the square of the dipole moment of the solute. The complex dielectric constant of a solution of polar solute in a nonpolar solvent can be represented by

$$\epsilon = \epsilon' - \mathrm{i}\epsilon'' \tag{3}$$

where the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant are proportional to solute concentration, C_2.[58]

$$\epsilon' = \epsilon_0 + a'C_2 \tag{4}$$

$$\epsilon'' = a''C_2 \tag{5}$$

Here, ϵ_0 is the dielectric constant of the pure solvent. The value of ϵ'' can also be given by[59]

$$\epsilon'' = A[S]\mu^2 g(\omega\tau) \tag{6}$$

where $[S]$ and μ are, respectively, the molar concentration of solute and its dipole moment. The constant A is given by

$$A = \frac{(\epsilon_0 + 2)^2(4000\pi)}{27k_\mathrm{B}TN_\mathrm{A}} \tag{7}$$

with T the absolute temperature, k_B the Boltzmann constant, and N_A Avogadro's number.

The frequency-dependent function, $g(\omega\tau)$, is given by

$$g(\omega\tau) = \omega\tau/(1 + \omega^2\tau^2) \tag{8}$$

for Debye-type relaxation of molecules with rotational relaxation time τ at an angular frequency of the microwave field ω. However, this function should not be taken literally, as a distribution of relaxation times is usually observed even for rigid molecules. The actual value of g is determined by measurement on the ground-state of the molecules (see below).

The microwave loss, L, from the microwave cavity is given by

$$L = \frac{\int_\mathrm{sample} \epsilon'' E^2\,\mathrm{d}v}{\int_\mathrm{cavity} E^2\,\mathrm{d}v} = \eta\epsilon'' \tag{9}$$

where η is a filling factor. From eq 8, it is evident that the maximum loss is produced only when $\omega\tau \sim 1$; however, the function is not strongly peaked, and a range of microwave frequencies will work for the solvents and the size of molecules under consideration. The frequency of ~9 GHz is convenient because of the ready availability and convenient size of the waveguide.

Two measurements are necessary. The first, a static measurement, is carried out on the ground state of the sample. The cavity, with a cell filled only with solvent inserted in it, is adjusted to be near to critically coupling, and then the reflected power is measured as a function of solute concentration. The function

$$f(P) = [1 - (P_r/P_0)^{1/2}]^{-1} = (1 + \beta^{-1})/2 + \beta^{-1}Q_0L/2 \qquad (10)$$

where $\beta^{-1} = Q_x/Q_0$ (Q_0 and Q_x are the Q values of the unloaded cavity and that due to external coupling, respectively), is evaluated for several concentrations of solute. The slope of the line, G, describing $f(P)$ vs [S] (L is proportional to [S]) is determined and β^{-1} eliminated by use of the intercept. When the measurements are made with the same cavity and cell for a new compound (2) as well as a reference compound (1), the quotient of the two slopes reduces to

$$\frac{\mu_2^{\,2}G_1}{\mu_1^{\,2}G_2} = \frac{g_1(\omega\tau)}{g_2(\omega\tau)} \qquad (11)$$

Hence, it is possible to determine absolute values of g($\omega\tau$) when the ground-state dipole moments of the two compounds and the value of g for the reference compound are known. Values of g for DPCP in benzene and 1,4-dioxane have been determined.[13]

The detector (balanced mixer) in the apparatus used for the transient measurements responds linearly to changes in the electric field amplitude (V_r), not the microwave power. The equation for the change ΔV_r caused by a change in loss, L, corresponding to the photolytically induced decrease in ground-state concentration and consequent formation of excited state with a different dipole moment, is

$$\Delta V_r/V_0 = -\beta^{-1}Q_0\Delta L/2 \qquad (12)$$

where V_0 is the initial field amplitude and β^{-1} is near unity. If the same cavity is used and the cell size and position are maintained constant, the ratio of the signals observed with the reference and the sample is given by

$$\frac{V_{s1}}{V_{s2}} = \frac{\beta_1^{\,-1}\,\Delta([S_1]\mu_1^{\,2})\,g_1(\omega\tau)}{\beta_2^{\,-1}\,\Delta([S_2]\mu_2^{\,2})\,g_2(\omega\tau)} \qquad (13)$$

assuming that the differences in samples are not sufficient to change the field distribution inside the cavity and, hence, to change η. The use of $g(\omega\tau)$ values for the ground state assumes that the direction of the dipole moment is the same in the ground and excited states and that the tumbling of the molecule is not changed. In view of the fact that the sizes of the molecules are not changed on excitation, their tumbling rates are expected to be essentially the same in the ground and excited states.

Combining this equation with eq 13, we can write

$$\frac{G_2V_{s1}}{G_1V_{s2}} = \frac{\beta_1^{\,-1}\,\Delta([S_1]\mu_1^{\,2})/\mu_1^{\,2}}{\beta_2^{\,-1}\,\Delta([S_2]\mu_2^{\,2})\,\Delta(\mu_2^{\,2})/\mu_2^{\,2}} \qquad (14)$$

This is the required equation used for the measurement of excited-state dipole moments. The quantities G and β are obtained, as stated earlier, from the ground-state microwave measurements using eq 12. Because the experiment is performed with a laser of constant intensity, the ratio $\Delta[S_1]/\Delta[S_2]$ is determined from the optical densities of the solutions (in this case, of singlet states). The reference compound used for our experiment is diphenylcyclopropenone (DPCP), which yields (with a quantum yield of unity) the nonpolar products, diphenylacetylene, and carbon monoxide.[12] The ground-state dipole moment of DPCP is reported to be 5.1 D.[60] Because, in our case, the reference compound, DPCP, transforms to nonpolar products, $\Delta(\mu_1^2)/\mu_1^2 = 1$. Hence, if the ground-state dipole moment of the unknown system is known, the excited-state dipole moment can be determined.

Instrumentation. The ground-state microwave measurements were carried out with a simplified circuit consisting of a 40-mW klystron (at about 9-GHz frequency), an attenuator, a 3-dB directional coupler, a circulator, and two detectors, each with an associated power meter. The same cavity and the coupling iris were used for both these and the transient measurements. The details of the circuitry for transient measurement can be found elsewhere.[12] The response time of the apparatus was determined from the cavity Q. This latter value was determined by measuring the frequency difference between points on each side of resonance at which the reflected power for the critically coupled cavity was one-half of the incident power. The normal response time of 36 ns was lowered to 8.9 ns by inserting a resistive plate along the short side of the cavity. The laser employed for photolysis was a Quanta-Ray PRO 230-10 Nd:YAG at the third harmonic (355 nm). The laser pulse energy was about 10 mJ/pulse over 1 cm^2. The pulse energy was limited by the possibility of ground-state depletion. Experiments at several pulse energies were used to verify that the dipole moments obtained did not depend on the laser dose. The accuracy of the final dipole moment values was estimated from the variation between replicate measurements to be about ±0.5 D. The laser dose was monitored while the samples were photolyzed to allow correction for any variation of laser intensity. The fluorescence lifetimes were measured on a single-photon-counting spectrofluorimeter equipped with a N_2 laser (Photon Technology International, Model GL3300) as the excitation source. Spectrophotometric measurements were made with a Shimadju spectrophotometer (UV 3101PC).

Results and Discussion

Photoinduced changes in the dielectric loss behavior of the coumarins have been studied in two nonpolar solvents, benzene and 1,4-dioxane. Even though the solubilities of the systems were adequate to allow time-resolved measurements in cyclohexane, the ground-state measurements, which require a higher concentration of the systems (typically 3−5 mM), could not be performed for most of the present systems because of low solubilities in cyclohexane. Typical changes in the laser-induced dielectric loss behavior are illustrated in Figure 1 (in benzene) and Figure 2 (in 1,4-dioxane) for two systems, a flexible system (**C152**) and a rigid one (**C153**), along with those for the reference compound, DPCP. Although the signals for coumarins and DPCP are shown in the same direction, it should be noted that, for all of the aminocoumarins, laser excitation led to an increase in the loss (indicating that $\Delta\mu$ values are positive) whereas that for the reference compound represents a decrease in the loss. The signal for the reference system has, therefore, been inverted in the figures for comparison. That the signals do not arise from any spurious effect, such as heating of the solution or the cavity, has been verified by performing blank experiments on benzene. Moreover, to make sure that only a change in dipole moment gives rise to the dielectric loss signal, it was verified that a benzene solution of anthracene (with a similar absorbance), a molecule for which $\Delta\mu$ is known to be negligible, does not show any signal under identical conditions.

As can be seen from the figures, the photoinduced loss signals for the aminocoumarins decay in a few nanoseconds, leaving

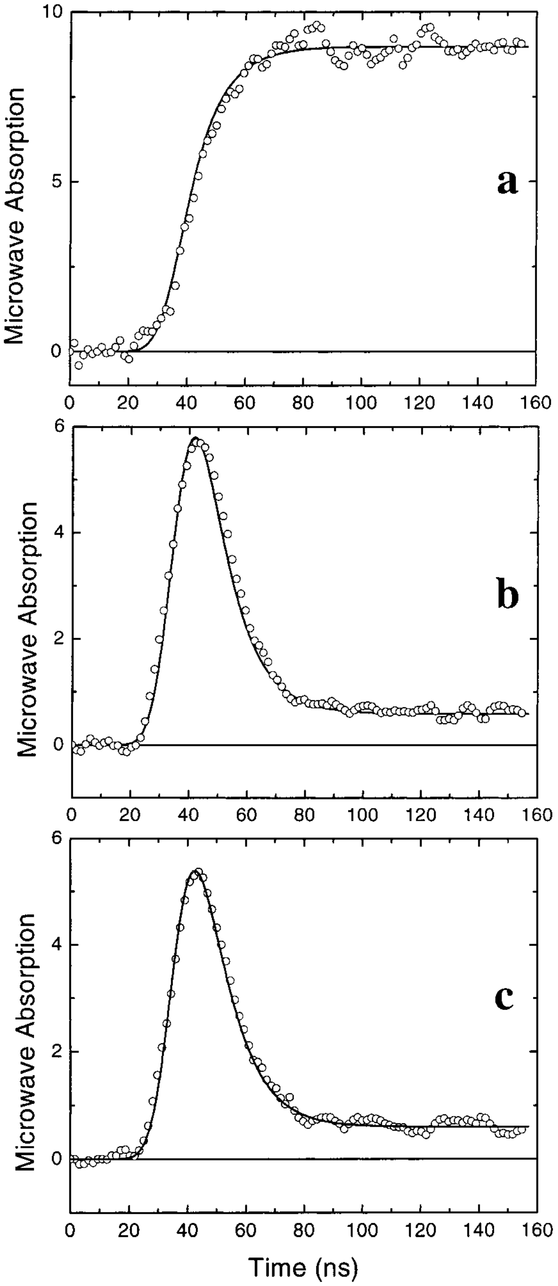


Figure 1. Time-resolved changes in the dielectric loss behavior of benzene solutions of (a) 3 mM DPCP, (b) argon-bubbled 0.8 mM **C152**, and (c) 1.0 mM **C153**. The curve for DPCP has been inverted and multiplied by $^1/_3$ for presentation. The solid curves are calculated by the method described in the text.

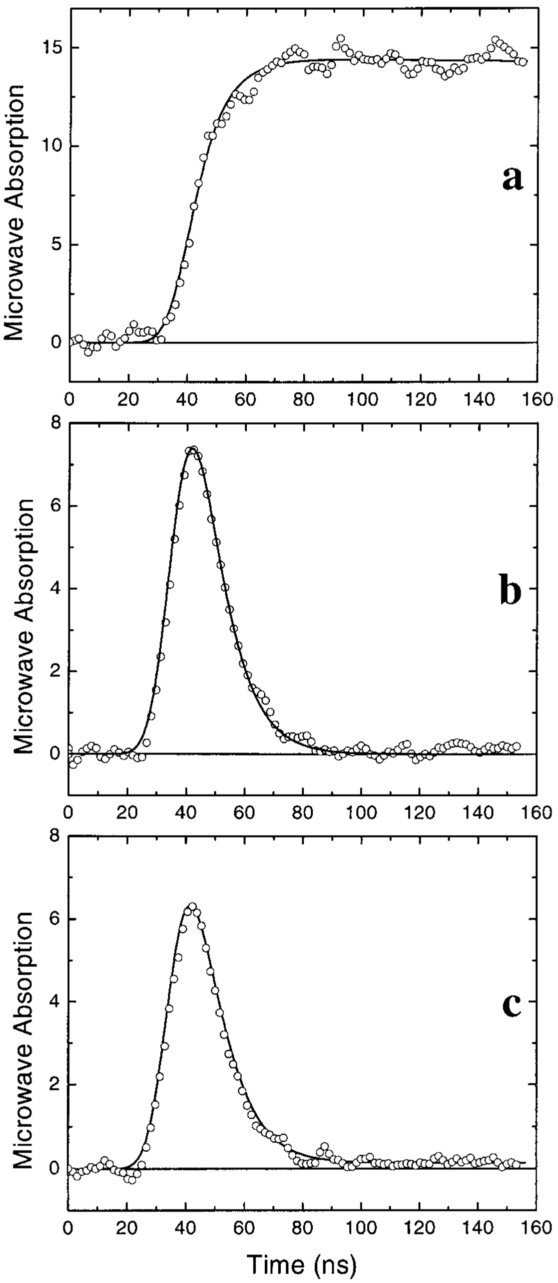


Figure 2. Time-resolved changes in the dielectric loss behavior of dioxane solutions of (a) 3 mM DPCP, (b) argon-bubbled 0.9 mM **C152**, and (c) 1.4 mM **C153**. The curve for DPCP has been inverted and multiplied by $^1/_3$ for presentation. The solid curves are calculated by the method described in the text.

some residual signal, in benzene, whereas in dioxane, the signals decay almost to the initial level. This residual signal is typically only ~1% of the total amplitude (see below for the analysis), and it decays on a longer time scale (several microseconds). Moreover, this long-lived minor component of the signal could not be observed in the presence of oxygen. The aminocoumarins are reported to be strongly fluorescent, with the fluorescence quantum yield very close to unity in some solvents.[17,42] The triplet yield is reported to be low (<0.05 in cyclohexane and <0.001 in ethanol for **C153**).[61] Taking consideration of these observations, the long-lived minor component is attributed to the triplet state of the molecules. This observation not only suggests that a small fraction of the molecules nonradiatively relax to the triplet state, but also indicates that the dipole moment of the molecules in the triplet state is larger than that of molecules in the ground state. Under the assumption that the dipole moment of the triplet state is comparable to that of the excited singlet, the triplet yields are estimated to be ~1%. A lower triplet yield in the more polar solvent dioxane is in accord with the trend reported by Jones et al.[61] However, other than the fact that the triplet yield of the aminocoumarins is low, the information available in the literature on the solvent dependence of the triplet yield is too limited to make any detailed comparison with data obtained by other techniques. We would also like to point out, in this context, that we did not observe any significant difference in the amplitude of the residual absorption for different derivatives in a given solvent.

The signal amplitudes (V_{s1} and V_{s2} in eq 14) required for the determination of the dipole moments of the molecules in the first excited singlet state have been obtained by fitting calculated

TABLE 1: Excited-State Dipole Moments of the Aminocoumarins with the Values of a Few Parameters Used for Their Estimation

solvent	sample	amplitude[a]	$g(\omega\tau)$	μ_g[b]	$\Delta(\mu^2)$	μ_e
benzene	**DPCP**	21.03	0.288	5.1[c]	$(5.1)^2$	0
	C1	44.65	0.345	6.35[d]	46.1	9.3
	C102	49.70	0.344	6.98	51.4	10.0
	C120	47.44	0.478	6.03[d]	35.3	8.5
	C151	64.66	0.383	4.59	60.1	9.0
	C152	74.00	0.317	5.71	83.2	10.8
	C153	64.24	0.260	6.55	87.9	11.4
dioxane	**DPCP**	13.50	0.193	5.1[c]	$(5.1)^2$	0
	C1	15.99	0.240	6.35[d]	24.9	8.1
	C102	24.88	0.136	6.98	68.2	10.8
	C120	16.93	0.193	6.03[d]	32.8	8.3
	C151	22.45	0.114	4.59	73.4	9.7
	C152	30.04	0.105	5.71	106.3	11.8
	C153	23.67	0.089	6.55	98.9	11.9

[a] Value from curve fitting, corrected for differences in dose, cavity *Q* value, and absorbances. [b] Unless specifically mentioned, experimental μ_g values are collected from ref 39. [c] Reference 60. [d] Reference 41.

TABLE 2: Fluorescence Lifetimes of Aminocoumarin Derivatives in Benzene and 1,4-Dioxane

	lifetime (ns)	
compound	in benzene	in 1,4-dioxane
C1	2.4	3.0
C102	2.9	3.4
C120	2.4	3.1
C151	3.7	4.5
C152	4.2	4.9
C153	4.5	5.4

TABLE 3: Change in the Dipole Moment ($\Delta\mu$)[a] on Electronic Excitation of the 7-Aminocoumarins as Obtained by Various Methods

	$\Delta\mu$			
sample	this work[b]	others	method	ref
C1	2.9 (1.7)	1.4	AM1	41
		7.3−7.8	electrooptic	34
		1.6−10.8	PPP, solvatochromism	37
		1.6−2.5	solvatochromism	57
		1.5−3.5	AM1, solvatochromism	38
		7.0	solvatochromism	40
C102	3.0 (3.8)	3.7	AM1	41
		1.8−3.7	AM1, solvatochromism	38
C120	2.4 (2.3)	2.2	AM1	41
		4.1−6.2	electrooptic	34
		1.7−7.9	PPP, solvatochromism	37
		1.6−2.9	solvatochromism	57
		1.4−2.2	AM1, solvatochromism	37
		6.1	solvatochromism	40
C151	4.4 (5.1)	5.2	AM1	41
		1.7−2.6	PM3, solvatochromism	38
		6.3	solvatochromism	40
C152	5.1 (6.1)	6.8	AM1	41
		1.9−4.0	PM3, solvatochromism	38
		8.1	solvatochromism	40
C153	4.9 (5.4)	7.0	AM1	41
		2.3−4.5	PM3, solvatochromism	38
		4.4−7.0	ab initio, electrooptic	33
		7.3−9.6	electrooptic	34,35
		6.3	solvatochromism	40
		7.9	MNDO	20
		8.5−9.5	transient dc photoconductivity	36

[a] The accuracy of the numbers reported here depends on the accuracy of the μ_g values. The error involved in the measurement of μ_e is typically ±0.5 D. [b] Values measured in benzene; the numbers within parentheses are those obtained in 1,4-dioxane.

curves to the formation−decay data. The curves were generated by numerical integration of an appropriate differential equation, taking into consideration the pulse shape of the excitation laser (12-ns full-width half-maximum Gaussian), the response time of the apparatus (8.9 ns), and the fluorescence lifetimes of the systems. Because the fluorescence lifetimes are shorter than the laser pulse width and instrument response time, the actual amplitudes are considerably larger than the peak heights shown in the figures. The calculation also allowed for intersystem crossing to form some triplet-state molecules. The residual signal attributed to the triplet state is relatively large because it does not decay on this time scale. The quality of the agreement of the calculated curves is depicted in Figures 1 and 2, and the signal amplitudes are collected in Table 1. The fluorescence lifetimes of the systems have been measured in benzene and dioxane, and the values are shown in Table 2. The fluorescence lifetimes of the trifluoromethyl derivatives are found to be higher than those for the methyl derivatives. This observation and the absolute values of the lifetimes are consistent with the literature.[40,42]

Table 1 summarizes some of the parameters used for the evaluation of the excited-state dipole moments, along with the final values. The ground-state dipole moments (μ_g), required for the estimation of the μ_e values, have been used from the existing literature. The experimental values have been used where available. In the absence of any experimental values, AM1-calculated values have been used. The results can be summarized as follows: First, the excited-state dipole moments of the aminocoumarins are higher than those for the ground state. Second, unlike the case for the ground state, the excited-state dipole moments of the 4-trifluoromethyl-substituted derivatives are slightly higher than those for the 4-methyl analogues. Third, the dipole moments of the structurally rigid systems are not very different from those of the flexible systems. Fourth, the excited-state dipole moment of any given system in benzene is not very different from that in the more polar solvent, 1,4-dioxane.

Table 3 compiles our results along with those obtained by various other techniques to enable a comparison. It is evident from this table that, among various theoretical calculations, $\Delta\mu$ values obtained by AM1 method[41] (also, ab initio calculation with the 3-21G basis set)[33] are closest to the values obtained by us. This is perhaps understandable when the fact that the AM1 Hamiltonian is better parametrized for polar and excited-state systems is taken into consideration. The $\Delta\mu$ values obtained by both electrooptical[34,35] and transient dc photoconductivity[36] measurements are significantly higher than those obtained by us. It should be noted that the present method, in which $\Delta\mu$ is related to the amplitude of the signal, is much more direct than the two other methods, in which $\Delta\mu$ is related to the shape of the signal. Moreover, the present method does not involve assumptions such as a spherical cavity, which may not be valid for many systems, and also, the number of assumptions is relatively lower than that in other methods. In light of the above, the values reported here and the conclusions arrived at on the basis of the present measurements are expected to be more reliable than those made earlier.

Our data clearly suggest that the aminocoumarins do fluoresce from a state that is more polar than the ground state. However, the magnitude of the change in the dipole moment is not so large that it is necessary to assume that the fluorescence originates from a TICT state. The excited-state dipole moments of the TICT state of these systems are expected between 15 and 21 D.[40] On the other hand, the estimated values obtained by us lie between 8 and 12 D only. The fact that the μ_e values of the rigid systems, **C102** and **C153,** in which no twisting of the dialkylamino moiety around the C−N bond is possible, are very similar to those obtained for the flexible ones clearly substantiates our conclusion. Therefore, the low-lying zwitterionic, TICT state of the systems, if there is any, must be nonfluorescent. Moreover, the results presented in Table 1 show that the excited-state dipole moments of the systems in benzene and the relatively more polar solvent dioxane are rather similar. Had there been a close-lying highly polar TICT state just above the relatively less polar emitting state, then one would have expected an increase in the excited-state dipole moment with an increase in the solvent polarity. As that is not the case, we can also conclude that the TICT state does not play any role in dictating the photophysics of the aminocoumarins in media such as benzene and 1,4-dioxane. Close proximity of two states of different symmetry (other than the TICT state) in coumarins, **C153** in particular, is an issue that has been debated for some time.[18,20,26,27,41] The literature contains reports supporting as well as contradicting this idea. This is an important issue that determines how good a fluorescent system is in probing solvation dynamics. Our measurements do not provide any indication of the presence of two close-lying states. It is to be noted that our observation is in accordance with studies of transition moments recently made by Lewis and Maroncelli,[25] in which a much wider solvent polarity range has been probed.

In summary, we have measured the excited-state dipole moment of several aminocoumarins from a quantitative analysis of the time-resolved dielectric loss signal. This measurement provides perhaps the most reliable values of the dipole moments of the present systems, used extensively in the study of solvation dynamics. The results indicate that the change in dipole moment on electronic excitation is relatively small and that the fluorescence of these dyes originates from a state, which, although more polar than the ground state, is not the highly dipolar zwitterionic or TICT state.

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