

Planar and twisted intramolecular charge transfer states of the excited proton transfer products of aminocoumarins

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Received 10 November 1993; accepted 15 December 1994

Abstract

The excited state proton transfer (ESPT) reaction of aminocoumarins containing primary (**Ia**, **If**), secondary (**Ib**, **Ic**) and tertiary (**Id**, **Ie** and **Ila**, **Ilb**) 7-amino groups was studied. The limiting value of the fluorescence quantum yield (ϕ'_{∞}) of the ESPT product of the 7-aminocoumarins **Id** and **Ie**, containing an unfastened tertiary amino group, is unusually low in polar solvents (ethanol (EtOH), dimethylsulphoxide (DMSO)) in contrast with 7-aminocoumarins **Ia–Ic** and **Ilb**. A decrease in solvent polarity results in a strong (more than 40-fold in cyclohexane) increase in ϕ'_{∞} , probably due to a decrease in the rate of non-fluorescent, cationic, twisted intramolecular charge transfer (TICT) state formation.

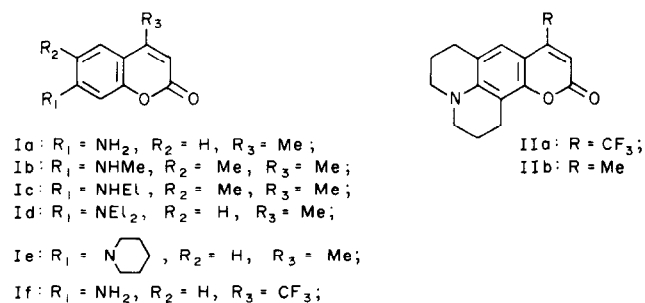
Keywords: Planar intramolecular charge transfer states; Twisted intramolecular charge transfer states; Excited proton transfer products; Aminocoumarins

1. Introduction

Oxoaromatic compounds are weak organic bases and their basicity essentially increases on excitation [1]. Derivatives of 7-aminocoumarin have the largest excited state basicities of the oxoaromatic compounds. The excited state protonation of coumarin **Ilb** derivatives in protic solvents is an irreversible diffusion-limited process [2,3]. The protonation in such systems is carried out by a solvated proton. The excited state proton transfer (ESPT) products of 7-aminocoumarins containing primary (**Ia**), secondary (**Ic**) and fastened (having a rigid structure to prevent amino group rotation) tertiary (**Ilb**) amino groups fluoresce effectively. However, the ESPT product of a 7-aminocoumarin containing an unfastened tertiary amino group (**Id**) does not fluoresce [4]. The fluorescence quantum yield of the ESPT product (ϕ'_{∞}) of **Ilb** is slightly dependent on the substitution in the pyrone ring and the nature of the solvent [5]. The anomalously low ϕ'_{∞} value for the aminocoumarin containing an unfastened tertiary amino group may be caused by the peculiarities of the substituted amino group structure. The introduction of alkyl substituents into the amino group of **Ia** results in a change in the Brønsted basicity and an increase in the probability of twisted intramolecular charge transfer (TICT) state formation. The formation of a non-fluorescent TICT state has

been postulated in a number of systems (diethylamino derivatives of benzopyrillium salts [6], 7-diethylaminocoumarins [7] and 4-dimethylaminonaphthalimides [8]). In such systems, the fluorescence quantum yield increases strongly as the solvent polarity decreases [6–9] due to the increase in the TICT state formation barrier.

In this study, the basicity of **Ia–If**, **Ila** and **Ilb** (see Scheme 1) in the ground state and the efficiency of the ESPT reaction of **I** and **II** with strong acids (H_2SO_4 , CF_3COOH) in ethanol (EtOH), tetrahydrofuran (THF), dimethylsulphoxide (DMSO), 1,2-dichloroethane ($C_2H_4Cl_2$) and cyclohexane (cyclo- C_6H_{12}) have been investigated in order to determine the cause of the low fluorescence efficiency of the ESPT product of the 7-aminocoumarin containing an unfastened tertiary amino group.



Scheme 1.

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2. Experimental details

The absorption spectra were recorded on a UV-3100 spectrophotometer; the fluorescence spectra were recorded on an Elumin-2M spectrofluorometer. The fluorescence quantum yield was measured by comparing the areas under the corrected fluorescence spectra of the fluorophore and a solution of quinine bisulphate in 1 N sulphuric acid ($\phi_f = 0.546$ [10]) without correction for the refractive index of the solvent. The luminescence data of the photoreaction products and the rate constants of fluorescence quenching of the aminocoumarins were determined using the home-generated software "SPECTR" and "EQUIL". The measurements were carried out at 20 °C. The concentration of the 7-aminocoumarins was approximately 2×10^{-5} M. The solvents were purified and dried according to the methods given in Ref. [11].

3. Results and discussion

The addition of H_2SO_4 decreases the intensity of the absorption spectra of ethanolic solutions of **Ia–If**, **IIa** and **IIb** and causes the short-wavelength band, attributed to molecules with the amino group protonated in the ground state, to appear. The addition of H_2SO_4 also decreases the fluorescence intensity of the neutral form of **Ia–Ic**, **If**, **IIa** and **IIb** and causes the protonated C=O group cation fluorescence to appear in the long-wavelength region (Fig. 1). The excitation of such systems was carried out at the absorption band of the neutral form where the cation with a protonated 7-amino group does not absorb. An isoemissive point exists in the fluorescence spectra. The excitation spectra of both fluorescence bands are practically identical and similar to the absorption spectrum of the initial form. On excitation of **Id** and **Ie** in EtOH at the absorption band of the neutral form, the fluorescence quenching of the initial form by H_2SO_4 takes place, but the fluorescence of the ESPT product is absent.

On addition of CF_3COOH to solutions of **Id** in DMSO, $C_2H_4Cl_2$ and THF and to solutions of **Ie** in THF, a similar short-wavelength shift of the absorption spectra takes place. In cyclo- C_6H_{12} , in the presence of CF_3COOH , a small (approximately 15 nm) long-wavelength shift of the absorption spectrum of **Id** is observed (Fig. 2). This shift is caused by the formation of a hydrogen-bonded complex between the C=O group of **Id** and the OH group of CF_3COOH . The decrease in **Id** absorbance in the red (Fig. 2) is associated with protonation of the N atom of **Id**. The long-wavelength fluorescence band which appears in acidified solutions of **Id** and **Ie** can be attributed to the emission of the protonated C=O group cation.

The acid–base interaction of 7-aminocoumarins (B) in protic solvents is shown in Scheme 2 [3]:

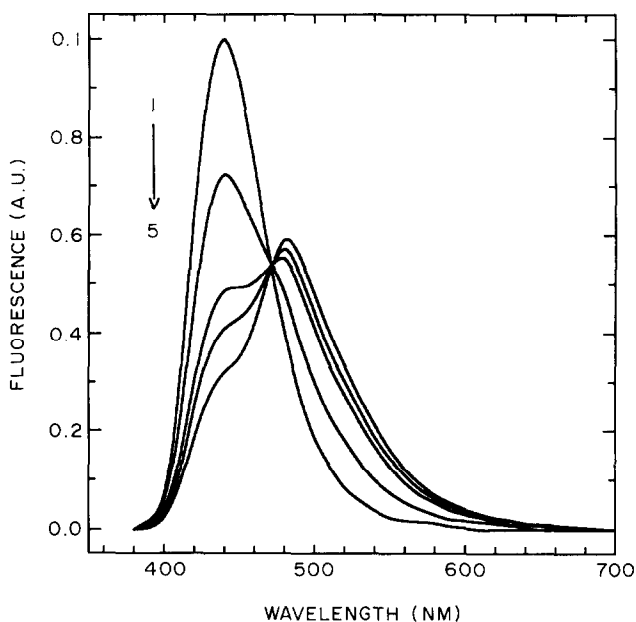


Fig. 1. Fluorescence spectra of **Ic** in EtOH at 20 °C. H_2SO_4 concentration: 0 (1), 0.0369 (2), 0.107 (3), 0.141 (4), 0.205 (5) M. Excitation wavelength, 350 nm.

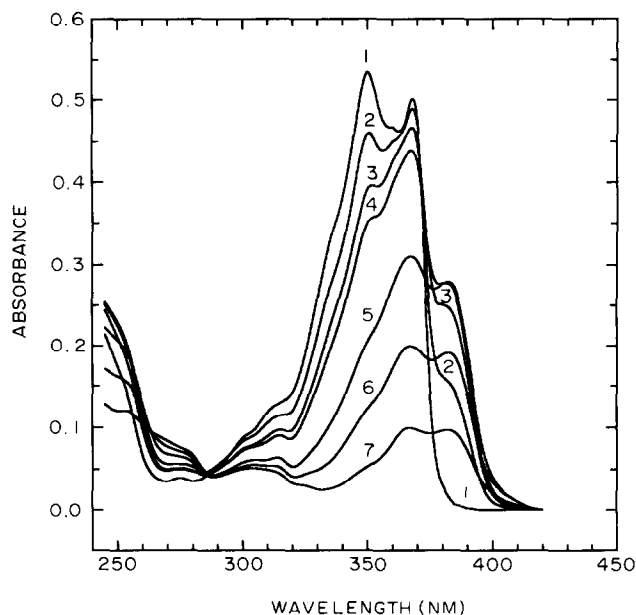
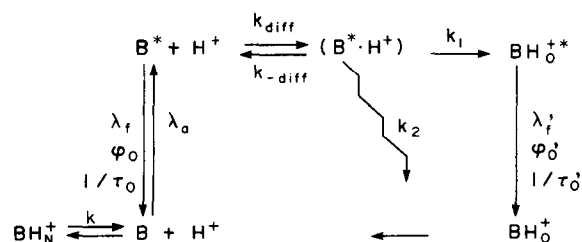


Fig. 2. Absorption spectra of **Id** in cyclohexane at 20 °C. CF_3COOH concentration: 0 (1), 0.0032 (2), 0.0040 (3), 0.0064 (4), 0.0103 (5), 0.0141 (6), 0.0179 (7) M.



Scheme 2.

where K is the equilibrium constant of the ground state protonation of the 7-aminocoumarin (to the nitrogen atom of the amino group), $(B^* \cdot H^+)$ denotes the encounter complex of the reagents, ϕ_0 and τ_0 are the fluorescence quantum yield and fluorescence lifetime of B respectively, ϕ'_0 and τ'_0 are the fluorescence quantum yield and lifetime respectively of the photoreaction product BH_0^{+*} on excitation from the ground state, k_{diff} and k_{-diff} are the rate constants of encounter complex formation and dissociation and k_1 and k_2 are the rate constants of excited product formation and radiationless deactivation induced by the forward reaction respectively.

For the given scheme, the fluorescence quantum yield of the initial form B can be calculated according to the Stern–Volmer equation

$$b_0/\phi = 1 + k_q\tau_0[H^+] \quad (1)$$

The ratio of the fluorescence quantum yields of the cation BH_0^+ and the initial form B is determined by the equation

$$b'/\phi = k_q\tau_0[H^+] \phi'_\infty/\phi_0 \quad (2)$$

where ϕ'_∞ is the limiting (acid concentration $\rightarrow \infty$) value of the fluorescence quantum yield of the ESPT product

$$b'_\infty = \phi'_0 k_1 / (k_1 + k_2) \quad (3)$$

The absorption and fluorescence data of the aminocoumarins and their ESPT products and the kinetic constants of Scheme 2 are given in Table 1. The similarity of the Stern–Volmer constants ($k_q\tau_0$) of the compounds studied to the $k_q\tau_0$ values of **IIb**, whose fluorescence is quenched by a dynamic mechanism [3], proves that, in EtOH, the fluorescence quenching of all the aminocoumarins investigated proceeds by a dynamic mechanism. The ESPT products of aminocoumarins containing primary (**Ia**, **If**), secondary (**Ib**, **Ic**) and fastened tertiary (**IIa**, **IIb**) amino groups fluoresce

($\phi'_\infty > 0.05$). In contrast, the ESPT products of 7-aminocoumarins containing unfastened tertiary amino groups (**Id**, **Ie**) do not fluoresce ($\phi'_\infty < 0.01$).

It can be seen (Table 1) that the ground state protonation constants K of **Ia** and **IIb** differ by more than 11-fold, but the ϕ'_∞ values of these compounds only differ slightly. On the other hand, the basicities of **Ia** and **Id** are practically the same, but the ϕ'_∞ values for the cations **IaH₀⁺** and **IdH₀⁺** differ by more than 1.5 times. Apparently, there is no clear correlation between the ground state basicity and the ϕ'_∞ values of the aminocoumarins.

The low ϕ'_∞ values of the aminocoumarins **Id** and **Ie** (Eq. (3)) may be caused either by the strong radiationless deactivation induced by the proton transfer reaction ($k_2 \gg k_1$) or by the low fluorescence quantum yield ϕ'_0 of the ESPT product. It can be seen from Table 1 that the value of the sum of the rate constants of proton transfer and induced radiationless deactivation (k_i) changes slightly in the series **Ia**, **Id** and **IIb**. We can assume that the values of k_1 and k_2 are also changed slightly in this series. In this case, the low ϕ'_∞ values of **IdH₀⁺** and **IeH₀⁺** are related to the low fluorescence quantum yield ϕ'_0 of these cations.

The similarity between the fluorescence results of the ESPT products of **Ia–Ic**, **If**, **IIa** and **IIb** indicates that the excited states of these aminocoumarins have a quasi-planar structure. The first excited state of the neutral aminocoumarin molecules is an intramolecular charge transfer (ICT) state [7,12]. We assume that the S_1 state of the ESPT product is also an ICT state since the protonated carbonyl group can be considered as a strong electron accepting substituent.

The excited state processes of the aminocoumarins containing unfastened tertiary amino groups are shown in Scheme 3:

Table 1
Absorption, fluorescence and ESPT reaction^a data of 7-aminocoumarins in EtOH

Compound	λ_a (nm)	ϕ_0	λ_f (nm)	ϕ'_∞ ^b (%)	λ'_f (nm)	τ_0 (ns)	K ^c (M ⁻¹)	$k_q\tau_0$ ^d (M ⁻¹)	k_i ^e (10 ⁹ s ⁻¹)
Ia	354	79	432	37	479	3.4 ^f	8.00	20.8	5.6
Ib	366	65	441	44	493	–	4.60	21.0	–
Ic	367	75	440	55	485	–	1.80	12.3	–
Id	376	56	450	<1	–	3.1 ^f	9.50	20.0	6.3
Ie	365	65	457	<1	–	–	20.9	43.0	–
If	383	68	485	12	534	5.0 ^g	1.20	2.84	0.32
IIa	426	54	536	5	590	3.4 ^f	–	6.85	1.3
IIb	390	80	471	45	530	4.4 ^h	0.71	20.9	4.8

^a With H₂SO₄.

^b Limiting (acid concentration $\rightarrow \infty$) value of the fluorescence quantum yield of the ESPT product.

^c Equilibrium constant of 7-aminocoumarin protonation to the N atom in the ground state.

^d k_q is the Stern–Volmer rate constant for the quenching of 7-aminocoumarin fluorescence by acid.

^e The sum of the rate constants of proton transfer and induced radiationless deactivation: $k_i = k_1 + k_2 = k_{-diff}k_q / (k_{diff} - k_q)$.

^f From Ref. [7].

^g From Ref. [12].

^h From Ref. [3].

Table 2
Absorption, fluorescence and ESPT reaction ^a of 7-aminocoumarins in different solvents

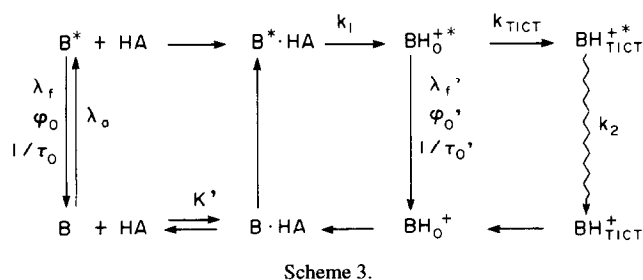
Aminocoumarin (solvent)	λ_a (nm)	ϕ_0 (%)	λ_f (nm)	ϕ'_∞ (%)	λ'_f (nm)	$k_q\tau_0^c$ (M ⁻¹)	$E_T(30)^d$ (kJ mol ⁻¹)
Id (EtOH)	376	56	450	<1	–	9.50	217
Id (DMSO)	374	59	440	<1	–	0.17	189
Id (C ₂ H ₄ Cl ₂)	371	44	427	3	480	61.8	173
Id (THF)	363	60	419	10	476	3.59	157
Id (cyclo-C ₆ H ₁₂)	–	38	394	38	418	–	129
Ie (THF)	360	66	423	11	478	5.52	157

^a With CF₃COOH.

^b Limiting (acid concentration → ∞) value of the fluorescence quantum yield of the ESPT product.

^c k_q is the Stern–Volmer rate constant for the quenching of 7-aminocoumarin fluorescence by acid.

^d Reichardt's solvent polarity parameter [13].



where K' is the ground state equilibrium constant for hydrogen-bonded complex ($B \cdot HA$) formation and k_{TICT} is the rate constant of TICT state formation. As shown in Table 2, the ϕ'_∞ value increases as the solvent polarity, described by the $E_T(30)$ parameter, decreases (more than 40-fold in cyclo-C₆H₁₂). In other words, the value of k_{TICT} rises and the reaction barrier height decreases as the solvent polarity increases. This means that the TICT state energy is changed to a greater extent than the ICT state energy. This unusual dependence of the barrier height of an ionic reaction on the solvent polarity (for the ions, the energy of the solvent–solute interaction is determined mainly by the ion–dipole interaction) can be explained by the different solvation energy of cations BH_0^{+*} and BH_{TICT}^{+*} as a consequence of the electron density redistribution during the reaction. In polar media, where cations BH_0^{+*} and BH_{TICT}^{+*} are free ions, it is caused by the different contributions of solute–solvent interactions of higher order (dipole, quadrupole, etc.) to the solvation energy of these cations. In low polarity media, in which BH_0^{+*} and BH_{TICT}^{+*} exist as ionic pairs with anion CF_3COO^- , the difference between the solvation energies of the ionic pairs $BH_0^{+*} \cdot ^-OOCF_3$ and $BH_{TICT}^{+*} \cdot ^-OOCF_3$ is related to the higher dipole moment of the $BH_{TICT}^{+*} \cdot ^-OOCF_3$ ionic pair as a consequence of charge transfer from the pyrone ring to the amino group as the TICT state is formed.

4. Conclusions

It has been shown that the limiting value of the fluorescence quantum yield (ϕ'_∞) of the ESPT product of 7-aminocoumarins **Id** and **Ie** containing unfastened tertiary amino groups is unusually low in polar solvents (EtOH, DMSO) in contrast

with 7-aminocoumarins **Ia–Ic** and **IIf**. A decrease in the solvent polarity results in a strong (more than 40-fold in cyclohexane) increase in ϕ'_∞ , probably because of the decrease in the rate of non-fluorescent cationic TICT state formation. The dependence of the barrier height of the ionic reaction on the solvent polarity can be explained by the different solvation energies of cations BH_0^{+*} and BH_{TICT}^{+*} as a consequence of electron density redistribution during cationic TICT state formation.

Acknowledgment

This work was supported by the Fundamental Investigations Fund (Russia).

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