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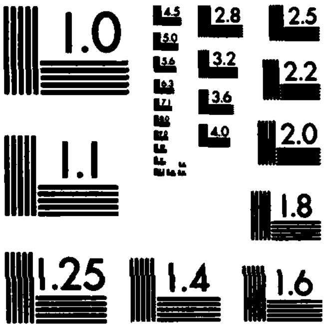

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Photophysical parameters have been determined for coumarin laser dyes in organic solvents and water. Fluorescence yields and lifetimes were sensitive to solvent polarity depending on subtle features of dye structure. Protic solvents were important in reducing emission yield for certain dyes. Radiative and non-radiative rates were obtained and trends analyzed in terms of dye structure, solvent properties, and medium temperature.

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SOLVENT EFFECTS ON EMISSION YIELD AND LIFETIME FOR COUMARIN LASER DYES. REQUIREMENTS FOR A ROTATORY DECAY MECHANISM

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Abstract

Photophysical parameters have been determined for coumarin laser dyes in a variety of organic solvents and including water and mixed media. The response of fluorescence emission yields and lifetimes to changes in solvent polarity was a sensitive function of substitution pattern for the coumarins. Most important were substituent influences which resulted in larger excited state dipole moments (for the fluorescent state), in restrictions of rotatory motion for the amine group at the 7-position, and the delocalization of excitation energy away from the coumarin moiety. For dyes displaying sharp reductions in emission yield and lifetime with increased solvent polarity, protic media and particularly water were most effective in inhibiting fluorescence although deuterium isotope effects (H_2O/D_2O) on photophysical parameters were minimal. The temperature dependence of emission yield and lifetime was measured for two solvent sensitive dyes in acetonitrile and in a highly viscous solvent, glycerol. The quenching of coumarin fluorescence by oxygen for dyes with lifetimes > 2 ns was also observed. The dominant photophysical features for coumarin dyes are discussed in terms of emission from an intramolecular charge-transfer (ICT) excited state and an important non-radiative decay path involving rotation of the amine functionality (7-position) leading to a twisted intramolecular CT state (TICT). This previously proposed non-radiative decay path is a subtle function of coumarin structure, solvent polarity and viscosity, and temperature, and is most sensitive to substituent patterns which localize excitation at the 7-amino group and which stabilize charge in the twisted zwitterionic (TICT) intermediate. The role of excited state bond orders involving the rotating group in determining the importance of interconversions of the type, ICT → TICT, is discussed.

It has been known for some time that the yield of fluorescence emission for 7-aminocoumarins (e.g., 1 - 11), the important class of laser dyes for the "blue-green" region, depends critically on the pattern of substitution about the amine function.[1,2] A similar trend ascribed to a non-radiative decay process observed for structures displaying an unrestricted amine moiety (e.g.,1 and 2, as compared to 3 and 4) has been also found for oxazine,[3] rhodamine,[4,5] and xanthene laser dyes.[1] Based on measurements of fluorescence yield and lifetime for coumarins of varied structure in solvents representing a wide range of polarity, a model of non-radiative decay was proposed[6,7] which employs a planar highly emissive intramolecular charge transfer (ICT) excited state capable of decay to a non-fluorescent twisted CT state (depicted simply below in terms of resonance forms, ICT → TICT).

The modes of formation and decay of highly polar excited state structures have received much recent attention.[8] The proposals concerning the rather large family of fascinating interconversions of the type, ICT → TICT, followed an early suggestion by Rotkiewicz, et al.,[9] and have been developed quite thoroughly by Grabowski, et. al.,[10] Rettig,[11] and Lippert.[12] A variety of structures displaying ICT excited state properties have now been investigated, including the legendary p-N,N-dimethylaminobenzonitrile (DMAB).[13] A battery of theoretical and experimental probes of structure-reactivity,[10,14] including ps time-resolved[15] and electrooptic emission measurements,[16] have been deployed.

The ICT-TICT rotatory decay model is reminiscent of a number of important photophysical phenomena which have been identified in the last decade, having to do with (1) "free rotors" as focal points for non-radiative deactivation,[17] (2) the "sudden polarization" of excited species,[18] and (3) the effects of drastic bond-order alteration on excitation.[19] The ramifications of non-radiative decay for polar excited states, and substituent and solvent effects thereon are quite broad and encompass issues concerning dye laser operation,[20] the behavior of fluorescence probes,[8,21] stereomutation of "push-pull" stilbenes, polyenes, and rhodopsin,[22] the light fastness of dyeing agents,[23] the effectiveness of photographic sensitizers,[24] and the development of molecular switching devices for optical data storage.[25]

In the present paper, we report more fully on our study of solvent effects on photophysical properties for the coumarins. In particular, we note that rotatory non-radiative decay, although important for a number of dyes in the most polar media, is not pervasive for the series and is in fact mitigated by a number of subtle structural influences and solvent effects which have been identified. This study is one of a series concerning coumarin dyes which includes investigation of mechanisms of photochemical degradation,[26] bimolecular excited state quenching and electron transfer reactions,[27] and behavior of dyes in amphiphilic media.[28]

Results

Absorption and emission measurements. Solvent effects. Photophysical properties of selected dyes are shown in Table 1, including fluorescence lifetimes measured by photon counting techniques as reported previously.[6,7] The spectral data include the following important features: (1) slight red shifts of absorption with increasing solvent polarity which correlate[7] with the solvent parameter, π^*, a measure of solvent polarity-polarizability;[29] (2) more dramatic reductions in emission frequency, again a smooth function of π^* and, the hydrogen bonding parameter, α,[30] (other solvent indexes have been correlated[31]); (3) a general broadening of the emission band in more polar and protic media (e.g., bandwidths, fwhm, for **1** of 2.9 and 3.1 kK for cyclohexane and water, respectively) and (4) extinction coefficients which range for most dyes between 16,000 and 22,000 M^{-1} cm^{-1} with exceptional absorption strength noted for 8 and 9 (ϵ = 55,000-70,000 M^{-1} cm^{-1}) (no dramatic trends in ϵ as a function of solvent for either group).

For the first series of dyes, values of emission yield and lifetime appropriate for argon purged samples were obtained (note details concerning the procedures and the importance of oxygen quenching in the Experimental Section), and the trends in photophysical parameters as a function of solvent are as follows. Coumarins 1 and 2 appear most susceptible to changes in solvent polarity in terms of emission yield and lifetime. With the addition of protic solvents and especially water these normally robust dyes can be rendered weakly fluorescent. For the homologous series, 6, 7 and 2, a regular trend having to do with the nature of substituents at the geometrically unrestricted amino group is developed. For dyes 3 - 5 exhibiting the amine function which is incapable of substantial rotation with respect to the coumarin aromatic ring, yields and lifetimes are altered somewhat in more polar media but the effects are much reduced compared to the "free rotor" dyes where as close to direct comparisons can be made.

The effect on emission properties of a polar but viscous solvent was evaluated. In glycerol a very large protic solvent red-shift was observed, but the extent of excited state stabilization (emission frequencies near that of water) did not translate into the sharp reduction in emission yield and lifetime found for the less viscous alcohol and water media. Most noticeable was the continuation of reduction in fluorescence yield (ethanol /water to glycerol) for dyes with more rigid structures (4 and 5) compared to the restoration of emission yield and lifetime for dyes with a flexible amine substituent (1 and 2).

With some indication of a viscosity dependence on fluorescence yield, comparisons were made of emission intensity for 50:50 ethanol/methanol solutions at room temperature and in a glass of the same solvent at 77 K. The intensity ratios were as follows: 2/4, 0.15 (RT), 0.90 (77 K); 2 /5, 0.12 (RT), 1.07 (77 K) (i.e., the non-radiative decay mechanism for 2 which is apparently unavailable to 4 and 5 can be eliminated at 77 K in a glassy solvent).

Following completion of this initial profile of solvent dependences, other classes of coumarin structures were inspected. For this series, 6 - 11, lifetimes were determined by a technique which depended on the diffusion controlled quenching of dye fluorescence by N,N-dimethylaniline (see Experimental Section). Emission yield and lifetime data are reported for air saturated samples (Table 2). The important result is that the changes so noticeable for the dyes (Table 1) with unrestricted dialkylamine functionality are absent in these related classes of dyes where either a delocalizing substituent is present at position-3 or where the substituent pattern about the amine function is altered.

Using familiar relationships shown below, rate constants were calculated (Table 3) for radiative, k_f, and non-radiative, k_{nd}, decay for dyes in which both yield and lifetime values were available.

$$k_f = \phi_f / \tau_f \qquad k_{nd} = (1 - \phi_f) / \tau_f$$

Temperature dependence of fluorescence yields and lifetimes. Photophysical properties for "free rotor" dyes and a rigid system were evaluated as a function of temperature, with results shown in Table 4. For

1 lifetimes had been previously measured[6] and rate constants obtained directly. Assuming a common value of 1.5×10^{8} s-1 for k_f, similar data could be generated for 2. Plots of ln k_d vs 1/T were linear ($r = 0.99$) and yielded for 1 (in glycerol) Arrhenius parameters, $A = 6 \times 10^{11}$ s-1 and E_a = 4.9 kcal/mol and for 2 (in acetonitrile), $A = 1 \times 10^{11}$ s-1 and E_a = 2.4 kcal/mol.

Mixed media. The effect of added water and change in pH. In view of the intimations of a specific interaction of the fluorescent coumarin state with solvent (particularly the importance of hydrogen bonding), a series of experiments employing mixed media was carried out. An effort to discover anomalous or dual emission associated either with specifically or differentially solvated excited species or in fact a second emission to be associated with a TICT excited species has already been reported.[6] (Generally, an excellent fit of single exponential decay curves to experimental data over 2-3 decades of photon counting was observed and lifetime measurements utilizing light filters at the "blue edge" vs "red edge" of emission suggested a single fluorescing species within rather strict limits of detection.[6])

Addition of water to organic solvents was of special interest. For coumarin 2 a general further broadening of the fluorescence band with no fundamental change in band shape (λ_f = 509 - 534 nm) and a regular reduction in fluorescence yield (ϕ_f = 0.090 - 0.023) were observed on changing the composition (0 - 90%, 10% increments) of water-ethanol solvent mixtures. Somewhat more dramatic was the addition of water to acetonitrile solutions of 1 and 3 resulting again in a regular red shift of absorption and changes in emission properties (Table 5). Shown also is the result of addition of D_2O in parallel experiments with 1 and 3.

Since acid-base reactions have been identified with some coumarins (the 7- hydroxycoumarins - the umbelliferone series[34] - but also including some aminocoumarins[1,35]), changes in pH within a moderate range were investigated. For 3 which fluoresces rather well in water (at its solubility limit of ca. 0.001 mM, Table 1), changes in absorption or emission maxima or in emission yield for aqueous solutions at pH 4.0, 7.0, and 10.0 were not detected.

Flash photolysis experiments. Triplet counting. To investigate the role of intersystem crossing in non-radiative deactivation, several dyes were subjected to flash irradiation using conventional equipment (xenon flash lamp, flash duration, 35 μs FWHM). Weak transient signals were observed for 1 in argon-purged acetonitrile, 85% acetonitrile /water or cyclohexane with an absorption profile (λ_{max} = 600-625 nm) similar to spectra which have been reported for 1 in ethanol[36] or in mixed EPA solvent.[37] The decay of transients from 1 was found to be first-order and consistent with a triplet lifetime of 120 - 180 μs in acetonitrile. A similar weak transient signal which decayed in the millisecond time scale was also observed for 8 in acetonitrile. On the other hand, transient absorption could not be detected for 2 or 4 under similar conditions where purging of oxygen from the flash cell was extensive.

Attempts were made to measure intersystem crossing yields using the triplet counting technique.[38] Glc analysis was performed on coumarin dye solutions containing 1,3-cyclohexadiene, a relatively low energy triplet counter which is known to undergo dimerization in the presence of a triplet sensitizer.[39] The coumarins with diene were irradiated in parallel with benzophenone solutions also containing triplet counter. The results for two solvents are shown in Table 6. The apparent failure of two dyes to produce triplets in a polar medium and only modestly in cyclohexane is not readily ascribed to an energy deficiency on the part of the coumarin triplets. Although their triplet energies are not precisely known (phosphorescence is not detected in low temperature glasses), indications of triplet location (ca. 50-55 kcal/mol) are found in the energy transfer data for the "ketocoumarins" having similar structures but for which intersystem crossing efficiencies are generally high.[40] At least moderate efficiency in thermoneutral or slightly endothermic energy transfer to cyclohexadiene (E_t, est. = 53 kcal/mol[39]) at high concentrations of quencher is expected.

Somewhat different behavior was observed for 1 dissolved in pure water. Flash irradiation of an aqueous saturated solution (ca. 0.01 mM) resulted in another weak transient now extending through much of the visible with a broad maximum which appeared to be shifted to ca. 700 nm. This observation, consistent with formation of the solvated electron[41] via photoejection from excited coumarin from either its singlet or triplet state,[42] was not repeated on similar flash photolysis of 2 in water.

Discussion

The alteration of the photophysics of coumarin[44] by substitution of an amine group in the 7-position is readily understood in terms of replacement of the conventional low-lying n,π^* and π,π^* states with an intramolecular charge-transfer excited state (ICT) which involves promotion of an electron from an orbital which is significantly weighted at the amine moiety (in Kasha's terminology, an $1_a \rightarrow \pi^*$ transition[45]). The enhancement of fluorescence at the expense of intersystem crossing with this substitution, and the additional effects of solvent are reminiscent of the trends observed for other coumarins substituted with donor groups including the furocoumarins,[46] and 4,4'-N,N-dimethylaminobenzophenone (Michler's ketone).[47]

The principal interest here in the aminocoumarins involves the precise identification of combinations of substituent pattern and solvent which conspire to inhibit luminescence. The main structural features are (1) the previously noted[1,6] annulation at the amine moiety which results in inhibited rotation (i.e., the undiminished fluorescence of 3, 4, and 5, vs. the comparable 1 and 2); (2) the role of an electron withdrawing group at position-4 which results in the most dramatic response to changes in solvent polarity for dyes displaying the unencumbered amine function (2 vs 1); (3) for the "free rotor" dyes, a dependence on nitrogen substituents (for NR_2, non-radiative decay rates follow the trend, R = ethyl > R = methyl > R = hydrogen); (4) a diminished tendency toward non-radiative decay for NH_2-(6) and NHR-subsituted dyes with additional ortho ring substituents (i.e., 10 and 11); and (5) a similar sustained fluorescence in polar solvents for otherwise susceptible dye structures displaying a delocalizing substituent at position-3 (benzthiazole, 8, or benzimidazole, 9, groups).

Where fluorescence yield and lifetime are both available, the solvent effect can be resolved in terms of influences on radiative and non- radiative decay constants (Table 3). Although a regular change in the fluorescence rate constant (ca. two-fold reduction in k_f in the most polar solvents) accounts for part of the alteration in fluorescence yield,[48] the stronger influence involves k_d, the non- radiative decay parameter which is increased by as much as two orders of magnitude in polar media.

The observed solvent influences might have been related to several established phenomena contributing to non-radiative deactivation. Addition of polar solvents (especially hydrogen-bonding solvents) might lead to discrete, stoichiometric excited complexes which display low emission yields.[49] However, discontinuous spectral shifts and sizeable solvent isotope effects have been frequently observed for solvent exciplexes,[50] in contrast to our findings. The results also argue against a major role for electron photoejection from excited coumarin singlets, despite the fact that the solvated electron may be a product of irradiation of 1 in water (vide supra).[42] The oxidation potentials measured for 1, 2, and 3 ($E_{1/2}$ = 1.09, 1.20, and 0.72 V vs SCE, acetonitrile[37]) should reveal a tendency for dye photoionization, but the trend is apparently ignored since the lifetime of 2 is most influenced by polar solvent and fluorescence remains robust for 3 in water.[42]

Solvent effects on the yield of intersystem crossing for related structures are known.[48] However, for the present series an increase in triplet yield which would be associated with enhanced non-radiative decay in more polar media could not be confirmed by flash detection of triplets or conventional triplet counting. Likewise, neither singlet self quenching, which leads to measureable reduction in fluorescence yield only at very high concentrations of dye (e.g., 0.01 M), nor singlet photochemistry which remains inefficient ($\phi = < 10^{-3}$) in polar solvents,[26] can account for the trends in non-radiative decay. Acid-base reaction which could be important in protic media appears excluded due to the absence of a pH dependence of fluorescence over a significant range. The latter has been confirmed in a recent study of 3 which revealed proton transfer only in rather acidic media (pH < 2.0).[35]

For the cases in which non-radiative decay is most robust (1 and 2), the previously proposed[6,10] ICT-TICT deactivation remains most attractive. The importance of this decay path is expected for polar media where charges in the fully developed zwitterion can be stabilized. The additional structural clues include the absence of the torsional decay route for rigid structures, 3 - 5, the substituent influence on developing positive (dependence on NR_2 for 2, 6, and 7) and negative (substitution in the lactone ring, 1 vs 2) charge.[51] The restoration of fluorescence for 1 and 2 in polar glasses is also consistent with the elimination of a rotatory decay mode.

The role of solvent motion in assisting non-radiative decay of excited states via a rotatory path or involving the evolution of polar (CT) excited species has received much recent attention. The exertion of a hydrodynamic drag or friction by solvent against a rotatory decay mode has been proposed as the primary influence on k_{nd} in a number of cases in which correlations of k_{nd} with bulk solvent viscosity could be made.[4a,11,52] The necessity of solvent motion to stabilize charge through dielectric relaxation has also been considered a feature controlling the rate of non-radiative decay.[53]

In the cases of 1 and 2 and their relatives, several observations suggest that these influences taken alone do not provide an adequate model for the observed solvent effects. Although viscosity can control decay of the coumarins in certain instances (inhibition in glassy matrices), further correlation is not found in the temperature dependence data. Thus, the barrier to decay for 2 in acetonitrile is 2.5 kcal/mol, compared to the activation energy of viscoocity for acetonitrile of 1.8 kcal/mol (from a plot of ln $(1/\eta)$ vs 1/T). On the other hand, the temperature dependence of k_{nd} for 1 in glycerol provides E_a = 4.9 kcal/mol, a value far less than the E_η value for glycerol (16.2 kcal/mol). Additionally, the decay rates for 2, 6, and 7 show an inverse dependence on the size of the amine rotor (faster decay for the larger rotor). In terms of solvent orientation polarization, values for dielectric relaxation times are considerably shorter (generally less than 0.5 ns for electronic polarization of low viscosity solvents at room temperature[55]) compared to the observed non-radiative decay times ($1/k_{nd}$ = > 0.5 ns) for the coumarins.

We prefer a mechanism in which viscosity is a contributor to the barrier for rotatory decay of the type, ICT - TICT , but is not the dominant feature. We note particularly the rough correlation of the Stokes' shift of fluorescence $(\nu_a - \nu_f)$ with the non-radiative decay rate. Thus, for 2, 1, and 8(9), values for the shift in polar solvents range around 5.0, 4.0, and 2.0-3.5 kK, respectively. This trend parallels a reduction in rate of non-radiative decay for dyes with uninhibited rotors in solvents of similar polarity and viscosity (compare, for example, data in Tables 1-3 for 50% ethanol solvent). We conclude that an important solvent influence for the coumarins centers around a narrowing of the energy gap between the emissive (planar ICT) excited state and the ground state.

Application of the energy gap law to rationalize trends for radiationless transitions is well documented including recent examples involving organic fluorescent dyes[54] and transition metal complexes[55]. Indeed, the effect of solvent on k_{nd} for the coumarins *which are restricted from rotatory decay* appears to involve a modest "gap law" influence (note data for 4, Table 3). For ICT-TICT rotatory decay, on the other hand, special features may be in force as illustrated using the Figure. The figure of merit is not the absolute value of the energy gap between S_o and S_1 (2, 8, and 9 have similar excitation energies, E_{oo}), but the extent to which solvent is called upon to stabilize an excited state dipole moment. Again comparing free rotor dyes, we note substantial differences in the nature of the electronic transition producing the emissive state (larger Stokes' shift but much smaller extinction coefficients for 1 and 2 compared to 8 and 9). The greater CT character for 1 and 2 is associated with substantial alteration of electron densities and bond orders[19] with localization of excitation at various sites within the dye structure. For dyes exhibiting fast decay (especially 2), localization at the amine function activates a rotor which insures that excited molecules travel to a favorable geometry for non-radiative decay to the ground state.

The consequences on reactivity (in general, radiationless decay) of the distribution of electronic excitation energy in organic molecules has been most extensively discussed by Zimmerman.[56] One protocol involves the estimation of changes in bond order following excitation (the construction of a "ΔP matrix" from MO coefficients), and the inspection of pathways which tend to reverse these bond order alterations (molecular distortions which reduce local excitations and convert electronic energy into vibrational energy).[56] In the present case, inspection of MO's available from calculations involving ICT systems [10,57] shows that an increase in N-C (7-position) bond order results from excitation (the allowed transition according to PPP-SCF-CI calculation[10]). It appears that excitation initially creates a barrier for rotational deactivation. However, this rotatory path is facilitated by charge-stabilizing substituent groups, by polar solvent, and by a restoration of some of the delocalization energy lost in developing a quinonoid structure (ICT) (the disappearance of local excitations involving enlarged $N-C_7$ and C_4-C_5 bond orders on rotation to TICT). A diminution in the energy gap between ground and excited states is required during rotation, since the N-C pi bond order is initially enhanced at the ICT geometry but reduced to zero ($\Delta P = 0$ with the ideal 90° twist) for the TICT structure. This rationale provides insight to the empirical "minimum overlap rule"[10β] which predicts the likelihood of intramolecular charge transfer between donor and acceptor moieties (and ICT-TICT behavior) for systems which have fixed twisted geometries or are capable of rotation.

The substituent and solvent effects noted here are therefore interpreted in terms of charge stabilizing influences which tend to diminish the barrier for torsional motion which is the most favorable distortion for bringing ground and excited surfaces into proximity.[58] The Stokes shift of fluorescence is an indicator of stabilization of partial charge in ICT but, moreover, a signature of the substituent and solvent influences on the fully charge separated TICT intermediate and the transition state leading to it (Figure). The decidedly different character of the transition for unconstrained but not freely rotating dyes (8 and 9) (smaller Stokes shift, vide supra) signals the absence of local excitation which is favorable to rotatory decay (i.e., the ICT structure is no longer appropriate and amine group rotation, albeit permitted, does not lead to excited state bond order alteration and energy surface proximity[57]).

In summary, the mechanism of radiationless decay proposed for coumarin laser dyes,[6,7] is restricted to those structures displaying an amine moiety (7-position) which is free to rotate and is alkylated for stabilization of incipient charge in a TICT intermediate (1 and 2 but not 6, 7, 10, and 11[58]). ICT-TICT rotational deactivation is also inhibited (8 and 9) when the low energy transition does not involve an intramolecular transfer of charge (from the amine function)[60] which is indicated by a large and solvent sensitive Stokes shift of fluorescence. Very polar solvents are required for robust rotatory decay with protic media (especially water) playing a special role, presumeably due to favorable interaction with TICT as recently reported[62] for the DMAB system

Extension of the present discussion to include other types of fluorescent dyes and to the operation of dyes under lasing conditions is indicated in several reports. Drexhage originally documented effects of rotatory deactivation for rhodamine dyes[1] and Snare, et. al., have discussed the solvent effects on rhodamine B fluorescence in terms of both an energy gap dependence and rotatory decay.[63] In addition, use of protic solvents appears to boost the gain of dye lasers[64] (large Stokes shift, but where rotatory decay is not enhanced), and a temperature dependence of deactivation can be exploited to improve peak lasing power as recently demonstrated for 1 and other "free rotor" dyes.[65]

Experimental Section

Materials. Coumarin 2 was prepared and purified according to a published procedure.[66] Coumarin 5 was a gift from Dr. R. L. Atkins.[67] The other coumarins, 1 - 11, were commercially available laser grade materials obtained from Eastman Kodak Co. or Exciton Chemical Co. and were used in most cases as received following tlc analysis for impurities (silica, ethyl acetate / hexane). Spectroquality organic solvents (MCB glass distilled) were used along with reagent grade glycerol and triply distilled water. Deuterium oxide (99.8% D) (MSD Isotopes) was used as received. Quinine sulfate dihydrate (Aldrich) was purified by recrystallization from water. 1,3-Cyclohexadiene (Aldrich) was distilled at atmospheric pressure immediately before use. Benzophenone was recrystallized three times from petroleum ether. N,N-Dimethylaniline (Aldrich) was treated with lithium aluminum hydride and freshly distilled at reduced pressure (20 mm) prior to use.

Fluorescence quantum yields. Emission spectra were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer equipped with a differential spectrum correction unit. Spectra were recorded at room temperature for air-saturated samples, and integrated intensities were obtained by cut-out-and-weigh. Relative integrated intensities were compared vs. the fluorescence standard, quinine sulfate, whose quantum efficiency was assumed to be 0.55 (1.0 N H_2SO_4).[68] Fluorescence quantum yields were calculated using a quadratic correction for refractive index of the solvent and a correction for per cent light absorbed by the samples. For these measurements dilute samples (ca. 10^{-5} M, maximum O. D. < 0.2) were employed with excitation at or near the absorption maximum determined using a Perkin-Elmer Model 552 spectrophotometer. To correct for oxygen quenching of fluorescence,[69,70] samples were purged with argon until no further increase in fluorescence intensity could be observed. The ratio of maximum intensities for purged vs undegassed samples (Table 7) was used to calculate fluorescence yields for air-free solutions (Table 1). Notably, rate constants calculated for oxygen quenching approximated the diffusion limited values (Table 7).

Fluorescence spectra at low temperatures were obtained using the fluorimeter cryostat accessory with the insertion of a 4 mm quartz sample tube (undegassed 50:50 ethanol-methanol solvent) into the specially equipped tip of a Dewar flask filled with liquid nitrogen. The solvent mixture used provided a clear, uniform glass at low temperature. The variable temperature fluorescence measurements were carried out using the thermostatted fluorimeter sample holder and an external water circulator. Corrected fluorescence intensities were recorded as relative quantum yields as a function of temperature and converted to absolute fluorescence efficiencies (Table 4) based on the values obtained at 20-21°C vs quinine sulfate.

Fluorescence lifetimes. Emission lifetimes for argon purged samples of **1**, **2**, **4**, and **5** were available from single photon counting measurements as described previously.[6,7] Lifetimes for **8** - **11** were determined using a fluorescence quenching technique. N,N-dimethylaniline (DMA) was used to quench emission from all the dyes in air saturated solutions. Using the Stern-Volmer relation, $I_o/I = 1 + k_q\tau[Q]$ and the known lifetimes for **1**, **2**, **4**, and **5** corrected for oxygen quenching (Table 7), average values for k_q were determined: $1.0 \pm 0.3 \times 10^{10}$ and $0.77 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1}, respectively, for acetonitrile and 50% ethanol-water. The narrow range of rate constants for quenching by DMA allowed use of these average values for k_q for **8** - **11**, assuming a consistent diffusion limited rate. The Stern-Volmer constants for the series were $k_q\tau$ = 31.5, 27.7, 35.1, and 76.7, respectively, and the calculated lifetimes are given in Table 2.

Triplet counting. Quantum yields of intersystem crossing were estimated using the triplet counting technique.[68] The reference system was the dimerization of 1,3-cyclohexadiene using benzophenone as triplet sensitizer.[69] Diene dimers were obtained by preparative photolysis and identified by nmr analysis as previously reported.[69] Samples of 0.01 M benzophenone or coumarin dye with 0.1 M cyclohexadiene were placed in 18 x 150 mm Pyrex tubes and after purging by argon for 15 min were irradiated in parallel using apparatus and procedures previously described.[70] The merry-go-round assembly was placed in a filter solution containing 50 g/l $NiSO_4$ and 0.2 g/l 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate which provided a bandpass of 340-370 nm for the Rayonet chamber reactor 3500A lamps. Cyclohexadiene dimers were analyzed on a Varian Model 3700 gas chromatograph equipped with an HP 3380A integrator and a 50 ft x 0.25

mm WCOT column (OV-17 liquid phase) operated at 120 using pentadecane as an internal standard. The quenching of coumarin singlets (fluorescence) by cyclohexadiene (0.1 M) was not observed.

Flash photolysis. Flash photolysis apparatus which consisted of a Xe flash lamp with ca. 35 μs duration (fwhm) has been described previously.[71] Argon-purged solutions of 10^{-5} M dye and a 22 cm Pyrex cell were employed. Photographs of oscilloscope traces were obtained to record % transmission values which were converted to transient absorbance. For comparison of the relative yield of transients, absorbance values were recorded at their maximum at the shortest practical times following lamp discharge (usually 100 μs following flash).

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42. Whether the suspected electron photoejection is mono- or biphotonic or whether the reaction has a singlet or triplet precursor has not been determined (the triplet spectrum is absent). That water is required for observation of photoionization is reminiscent of the (monophotonic) ionization behavior of anisoles.[43]

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48. a. The radiative decay constant, k_f gives only a fair correlation with V^3 (e.g., $r = 0.95$ for a plot of the values for 4). For a discussion, see Turro, N. J. "Modern Molecular Photochemistry" The Benjamin/ Cummings Publishing Co., Inc.: Reading, Massachusetts; 1978; p 87. b. The relatively high values of radiative decay and ϕ_f found even for polar media (and ascribed to ICT fluorescence) appear to preclude observation of the weak luminescence (a "dual fluorescence" observed in more polar solvents) of TICT intermediates

proposed for DMAB and related structures.[10,13]

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51. Relative stabilization of negative charge (for the lactone moiety) is indicated by the reduction potentials of *1* and *2*: −2.2 and −1.8 V vs SCE (acetonitrile).[27]

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57. Molecular orbitals from simple HMO calculations give a crude indication of the trends in change of electron density. For the parent 12-orbital, 14-electron system the HOMO and LUMO appear with coefficients as shown below. The shift of electron density away from nitrogen and to the lactone ring (especially C-4) and the increase in bond order (decrease in antibonding) at C_7-N and at $C_4 - C_{10}$ are notable ("charge flow" data from more sophisticated calculations for similar ICT systems are available[14a]) The substituent effects at nitrogen and at C_4 are thus predictable. To assess the bond order change at the rotating nitrogen position, ΔP is calculated for N-C_7, where $\Delta P = P^* - P_o$, the difference in bond orders for excited and ground configurations.[19,36] The value obtained, $\Delta P = 0.07$ is much greater for the pi system corresponding to *1*(*2*) than for the more delocalized 21-orbital, 24-pi electron system corresponding to *9* ($\Delta P = 0.01$).

HOMO LUMO

58. a. Pronounced reduction in the ground, excited state energy gap at the 90° geometry and the "charge flow" (charge separation) as a function of twist angle are confirmed in SCF calculations on DMAB and related systems.[14] b. As a reference point, the barriers to rotation for the ground state for dialkylamino substituted push-pull systems are 8-10 kcal/mol.[39] The excited state barrier for ICT → TICT appears early during rotation and is a fraction in size of these values. c. The presence of an ortho substituent as in *10* and *11* may require a "gearing" of rotatory motions and further reduction in decay rate.

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60. In the general case, the ICT state may not be low lying. A locally excited (LE) state may be initially populated and capable of configuration interaction and rotatory decay.[10a,13c,61]

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Table 1. Absorption and emission maxima and fluorescence quantum yields and lifetimes for selected coumarin dyes[a].

	Solvent	λ_a	λ_f	Φ_f	τ_f[b]
1	cyclohexane	350	395	0.49	2.8
	ethyl acetate	361	416	0.99	3.1
	acetonitrile	367	430	1.03	3.4
	ethanol	373	451	0.73	3.1
	50% ethanol	381	454	0.30	1.4
	20% ethanol	382	456	0.11	0.70
	water	380	456	0.055	
	glycerol	384	463	0.58	3.8
2	cyclohexane	376	433	1.04	4.1
	ethyl acetate	392	479	1.09	4.6
	acetonitrile	396	501	0.091	0.60
	ethanol	400	509	0.090	0.85
	50% ethanol	412	523	0.032	0.45
	water	406	528	0.011	
	glycerol	413	524	0.18	2.7
3	cyclohexane	361	407	1.05	2.6[c]
	acetonitrile	380	450	0.91	3.3[d]
	ethanol	387	473	0.95	4.5
	50% ethanol	396	477	1.02	
	water	396	489	0.66	5.9[e]

4	cyclohexane	393	455	0.90	4.3
	ethyl acetate	409	501	0.93	5.4
	acetonitrile	418	521	0.56	5.6
	ethanol	421	531	0.38	3.4
	50% ethanol	425	542	0.38	4.7
	water	430	549	0.12	
	glycerol	434	546	0.22	3.5
5	cyclohexane	382	439	0.98	4.2
	acetonitrile	405	510	0.87	5.6
	ethanol	408	515	0.80	5.1
	50% ethanol	421	528	0.55	4.5
	glycerol	420	530	0.30	
6	acetonitrile	365	465	0.92	5.2
	50% ethanol	380	490	0.88	5.3
7	dioxane	384	470	0.94	
	acetonitrile	393	500	0.28	
	ethanol	396	520	0.21	
	50% ethanol	409	530	0.11	

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[a] Wavelengths in nm, τ values in ns; argon purged samples, room temperature.

[b] From photon counting measurements (ref. 6 except where noted).

[c] Ref. 32 and 33

[d] DMF solvent, ref. 32

[e] Ref. 33

Table 2. Photophysical data for selected coumarin dyes in polar media[a].

	Solvent	λ_a	λ_f	ϕ_f	τ_f
8	cyclohexane	437	475	0.60	
	acetonitrile	454	501	0.63	3.2
	50% ethanol	469	508	0.59	3.3
9	acetonitrile	403	480	0.67	2.8
	50% ethanol	419	485	0.35	2.3
10	acetonitrile	354	420	0.80	3.5
	50% ethanol	367	441	0.90	4.0
11	cyclohexane	368	420	0.65	
	acetonitrile	383	481	0.58	7.7
	50% ethanol	403	498	0.50	4.4

[a] Air-saturated samples at room temperature.

Table 3. Rate constants for radiative and non-radiative decay as a function of solvent[a].

	Solvent	k_f	k_{nd}
1	cyclohexane	1.8	1.8
	ethyl acetate	3.2	0.03
	acetonitrile	3.0	<0.1
	ethanol	2.3	0.87
	50% ethanol	2.1	5.0
	20% ethanol	1.6	13.
	glycerol	1.5	1.1
2	cyclohexane	2.5	<0.1
	ethyl acetate	2.4	<0.1
	acetonitrile	1.5	15.
	ethanol	1.1	11.
	50% ethanol	0.71	22.
	glycerol	0.67	3.0
4	cyclohexane	2.1	0.23
	ethyl acetate	1.7	0.13
	acetonitrile	1.0	0.79
	ethanol	1.1	1.8
	50% ethanol	0.81	1.3
	glycerol	0.63	2.2

5	cyclohexane	2.3	0.05
	acetonitrile	1.5	0.23
	ethanol	1.6	0.39
	50% ethanol	1.2	1.0
6	acetonitrile	1.8	0.15
	50% ethanol	1.7	0.23
8	acetonitrile	2.0	1.2
	50% ethanol	1.8	1.2
9	acetonitrile	2.4	1.2
	50% ethanol	1.5	2.8
10	acetonitrile	2.3	0.57
	50% ethanol	2.2	0.25
11	acetonitrile	0.75	0.55
	50% ethanol	1.1	1.1

---

[a] Rate constants in 10^8 s^{-1}

Table 4. Temperature dependence of photophysical parameters for 1 and 2[a].

	T(°C)	ϕ_f	τ_f(ns)	k_f	k_{nd}
1[b]	20	0.56	3.8	1.5	1.2
	40	0.41	3.1	1.3	1.9
	60	0.33	2.1	1.5	3.1
	80	0.23	1.5	1.5	5.0
2[c]	4	0.12			12.
	21	0.090			17.
	33	0.073			21.
	48	0.065			23.
	58	0.057			26.

[a] Rate constants in 10^8 s^{-1}

[b] Glycerol solvent

[c] Acetonitrile solvent; k_d values calculated assuming $k_f = 1.5 \times 10^8$ s^{-1}

Table 5. Intersystem crossing quantum yields for coumarin dyes.

	$\phi_t(C_6H_{12})$	$\phi_t(C_2H_5OH)$
1	0.30	0.006
2	0.043	<0.001
4	0.053	<0.001

Table 6. Coumarin fluorescence properties in acetonitrile/water[a]

[water],M	λ_f(nm)		I_0/I			
	1	3	1		3	
			H_2O	D_2O	H_2O	D_2O
1.0	435	453	1.13	1.11	1.04	1.06
3.0	441	459	1.40	1.41	1.09	1.16
5.0	445	463	1.80	1.69	1.13	1.16
7.0	447	466	2.10	2.00	1.14	1.16
9.0	447	470	2.42	2.20	1.17	1.17
11.0	448	470	2.65	2.57	1.22	1.21

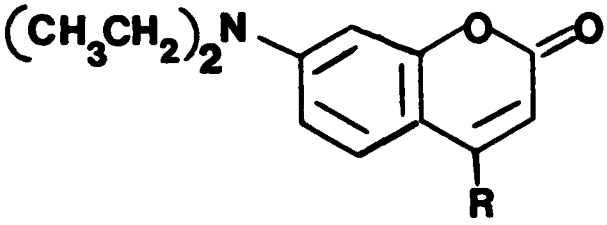
[a] Air saturated solution; [dye] = 10^{-5} M
I_0/I = ratio of fluorescnece intensities before and after addition of water with correction for sample dilution.

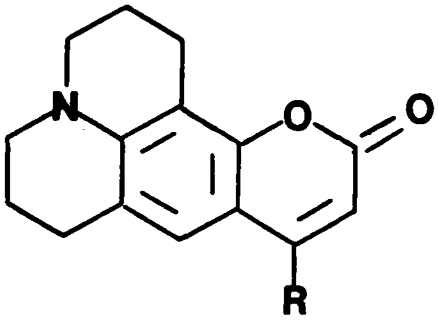
Table 7. Quenching of coumarin dye fluorescence by oxygen.

	Solvent	I_o/I[a]	k_q, $10^{10} M^{-1} s^{-1}$[b]
1	acetonitrile	1.21	2.5
	ethanol	1.07	1.1
2	acetonitrile	~ 1.00	
	ethanol	~ 1.00	
3	ethanol	1.22	2.4
4	cyclohexane	1.23	1.8
	acetonitrile	1.22	1.5
	ethanol	1.06	0.79

[a] Ratio of maximum fluorescence intensities for argon purged (I^o) and for air saturated (I) solutions.

[b] Calculated from $I^o/I = 1 + k_q\tau[O_2]$; τ values from Table 1 and $[O_2]$ taken from tabulated data (ref. 73).



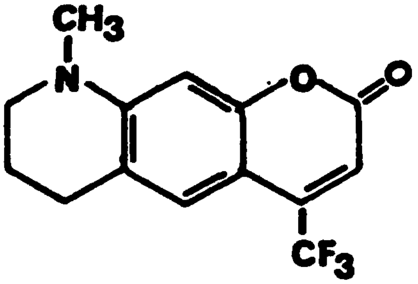


1, $R = CH_3$

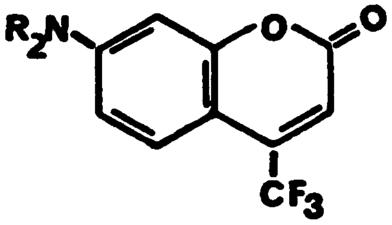
2, $R = CF_3$

3, $R = CH_3$

4, $R = CF_3$

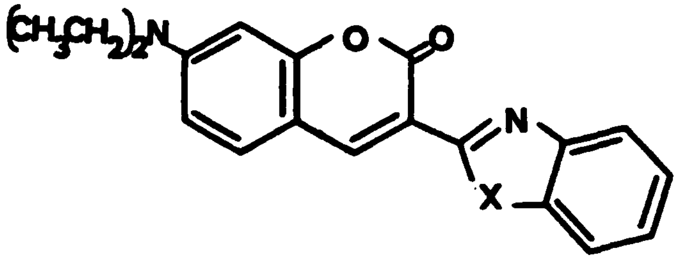


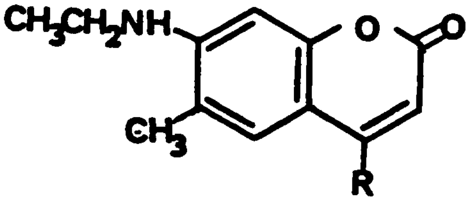
5



6, $R=H$

7, $R=CH_3$



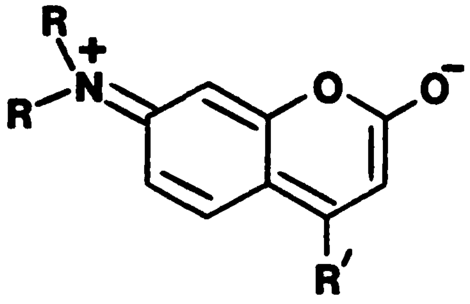


8, X = S

9, X = NCH$_3$

10, R = CH$_3$

11, R = CF$_3$



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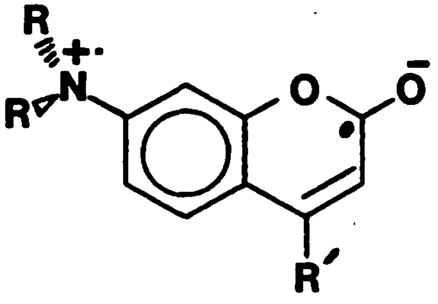

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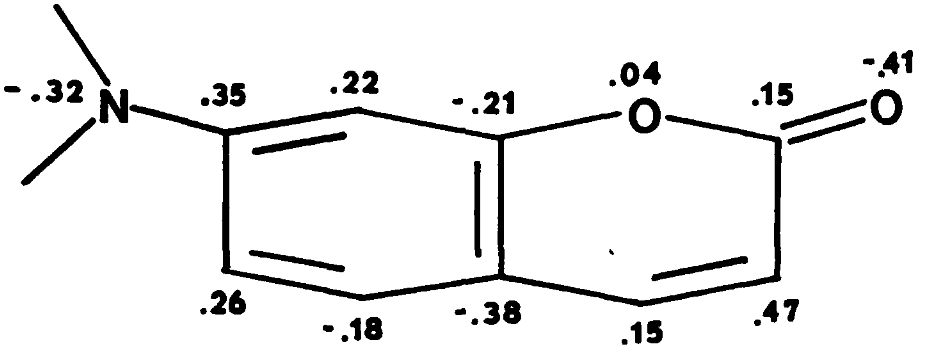
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N
.35
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O
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-.38
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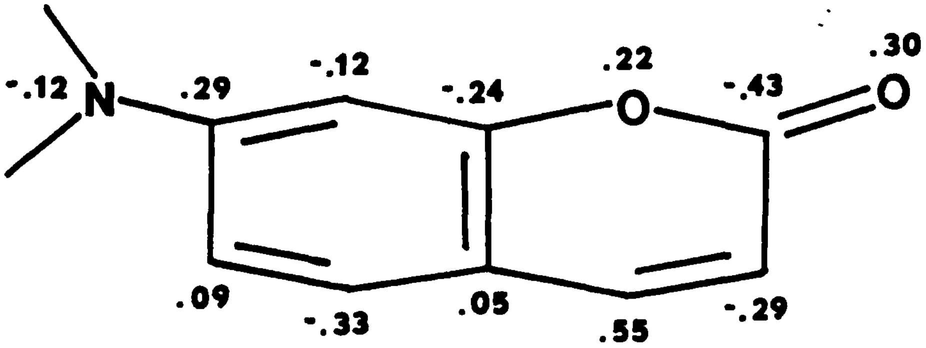
.47

HOMO


-.12
N
.29
-.12
-.24
.22
O
-.43
.30
O
.09
-.33
.05
.55
-.29

LUMO

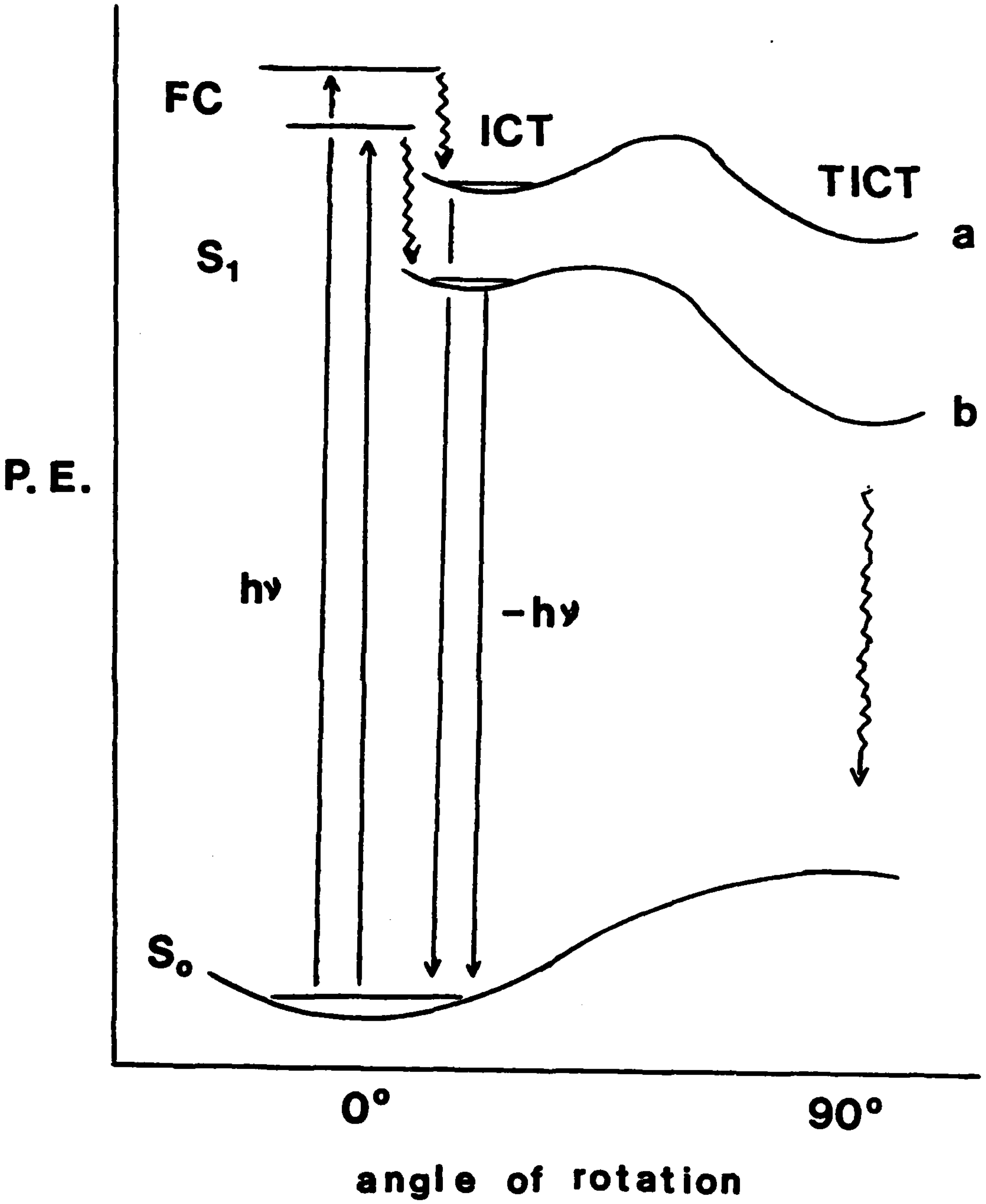


Figure. Potential energy surfaces for rotation at the amine function, depicting a Franck-Condon transition (FC), relaxation involving coordinates for solvation, and evolution of the planar emissive intramolecular CT state (ICT, 12) to the twisted conformation (TICT, 13). Energy relationships for the respective FC transitions, the barrier heights for rotation and the extent of stabilization of ICT (Stokes shift of fluorescence) and TICT are presented qualitatively for less polar (a) and more polar (b) solvents

END

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