SPECTRAL-LUMINESCENCE AND ACID-BASE PROPERTIES OF 4,7-DIAMINOCOUMARINS


The absorption and luminescence spectra of a series of 4,7-diaminocoumarins have been investigated in ethanol and acetonitrile solution. The $pK_a^I$ and $pK_a^{II}$ values for several of the compounds have been measured. It has been found that the site of primary protonation is the nitrogen atom in the 7-position, and that the second protonation reaction occurs at the lactone oxygen atom. The effects of steric and electronic factors on the spectral-luminescence and acid-base characteristics of these compounds are discussed.

We have previously reported [1] the synthesis of 4,7-diaminocoumarins I-XIX from the corresponding 4-chloro derivatives. Interest in these compounds has been stimulated by several factors. First of all, many of these 4,7-diaminocoumarins I-XIX are efficient luminophores, and several of these compounds (for example compounds I, III-V) also fluoresce in a short-wavelength region (400-440 nm) which is relatively rare for 7-aminocoumarins. In addition, compounds with similar structures (such as coumarins VI-IX) may have sharply different luminescence quantum yields. Second, according to [2], the excited singlet state ($S_1$) for 7-aminocoumarins is a charge transfer state (CT state, formula A). For this reason it was not clear a priori what influence a strong electron-donating substituent in the 4-position would have on the $\pi$-electron density distribution in the ground and excited states. In the case of 4,7-diaminocoumarins we cannot exclude the possibility of a different CT state in which charge transfer occurs from the 4-amino group (formula B).

Since many 4-aminocoumarins exhibit luminescence as well [3], the question arose which amino group would interact more efficiently with the lactone carbonyl group and, in general, on what factors do the spectral-luminescence properties of compounds I-XIX depend.

The absorption spectra of coumarins I-XIX in ethanol or acetonitrile solution contain, as expected, from three to five intense bands in the regions 245-260, 280-300, and 345-380 nm. The high oscillator strength values ($f \sim 0.4-0.8$), calculated according to [4] for long-wavelength absorption maxima in compounds I-XIX (Table 1), indicate that the corresponding electronic transitions are not forbidden. We assume that the absorption maximum in the 345-380 nm range in the spectra of coumarins I-XIX corresponds to a type A CT state; the same conclusion has been reached previously for close structural analogs of the coumarins in question, namely coumarin-1 (XX) and coumarin-102 (XXI) [2]. In our further discussions we shall limit ourselves primarily to consideration of the long-wavelength absorption maximum since, as has been explained, this band provides the most information and also correlates with the luminescence properties of the compounds. It is apparent from the data in Table 1 that replacement of a 4-methyl group by an amino group in the transition from compounds XX and XXI to 4,7-diaminocoumarin derivatives with similar structures (I-IX, XVIII, XIX), is accompanied by a hypsochromic shift of the absorption bands by 10-15 nm, and by a hypsofluoric shift of the emission bands by approximately 20-30 nm. The
greater sensitivity of the emission band to the effect of a substituent in the 4-position is not in conflict with our earlier-stated hypothesis concerning the existence of a type A CT state, in which the electron density in the lactone ring is enriched [5] and the lactone ring may also undergo strong perturbation as a result of interaction with the 4-amino group.

It is also interesting that substitution of a 4-monoalkylamino group by a 4-dialkylamino group, in the transition from compounds II-V, X, and XI to coumarins VI-IX, XII-XIV, is accompanied by a bathochromic shift of the long-wavelength absorption band by 7-19 nm, although the transition from 4-aminocoumarin I to 4-monoalkylcoumarins II-V does not produce any significant shift in this band. If we consider the normal increase in electron-donating properties of an amino group in the series NH$_2$ < NHAlk < NAlk$_2$, then we must conclude that this trend distorted in the case of 4,7-diaminocoumarins, in which a 4-dialkylamino group appears to act as a weaker electron-donating substituent than an NH$_2$ group. We feel that the factor responsible for this distortion is steric hindrance between the 4-dialkylamino group and the 5-H atom, which interferes with p-p conjugation in the N–C$_{(4)}$–C$_{(3)}$–C–O system. This type of steric strain or hindrance also increases even when the alkyl groups are fixed in a ring, such as, for instance, in the transition from compounds VI and VII to coumarins VIII and IX; the difference in the positions of the absorption maxima in these compounds is approximately 10 nm.

Introduction of an alkyl group in the 3-position exerts an analogous effect, leading to a bathochromic shift of the absorption band by 6-13 nm (compare compounds III, IV, IX, and X-XIV). We note, however, that in the 3,4-dialkyl-7-aminocoumarin series introduction of a 3-alkyl substituent is accompanied, in contrast, by a ~10 nm hypsochromic shift relative to 3-unsubstituted analogs [6]. Considering the similarity in the spectral characteristics of coumarin I and monoalkylaminocoumarins II-V, we conclude that the alkyl group in compounds II-V in their most favorable molecular conformations is spatially distant from the 5-H and in proximity to the 3-H atom. The H–N–C$_{(4)}$ fragment in coumarins I-V would therefore be expected to adopt similar structures. Supplementary confirmation of this conclusion is obtained from the PMR spectra of these compounds [1].

In the case of a substituent in the 7-position the steric factor is not expected to be significant, and so the 5-10 nm hypsochromic shift observed in the position of the long-wavelength absorption maximum in the transition from the 7-diethylaminocoumarins VI and IX to their 7-morpholino analogs XVI and XVII can be ascribed to the reduced electron-donating properties of the nitrogen atom in the 7-position [N$_{7}$]. Qualitative support for this conclusion concerning decreased electron-donating characteristics of a morpholino group relative to piperidino and diethylamino groups in the 7-position is provided by the basicity data for morpholine, piperidine, and diethylamine, whose pK$_{a}$ values are 8.33, 11.12, and 11.09, respectively [7]. Securing or fixing the 7-dialkylamino group in a julolidine fragment as in compounds XVIII and XIX is accompanied by a bathochromic shift of the absorption band by 15-20 nm relative to the 7-diethylamino derivatives VI and IX. An analogous trend has also been shown to be valid for coumarins XX and XXI.

The general principles delineated above for the positions of the long-wavelength absorption bands in the spectra of compounds I-XIX are characteristic of their emission bands as well (Table 1). Coumarin II appears to be an exception to this rule; its fluorescence maximum is shifted approximately 30 nm toward longer wavelength compared to the fluorescence maxima in compounds III-V. This effect may be due to steric hindrance of strain arising in the Si state between the tert-butyl group and the 3-H (or 4-H) atom; the steric strain, in turn, reduces the degree of electron-donating interaction between the substituent in the 4-position and the 7-amino group.

In order to understand the factors responsible for the wide variation in fluorescence quantum yields among the coumarins studied herein we have also investigated the low-temperature luminescence spectra of cumarins I, III, VI, IX, and XII. It was found that the fluorescence quantum yields for compounds I, III, VI, and XII under these conditions were substantially enhanced ($\phi_{F} = 0.8-0.9$), and exhibited a leveling-off effect. In contrast, however, the fluorescence quantum yield for coumarin IX was found to be largely unchanged at 77 K ($\phi_{F} = 0.56$). We conclude, therefore, that the fluorescence quenching effect observed for compounds VI, VII, and others at room temperature must be associated not with any electronic influence of the 4-dialkylamino group, but rather with vibrational loss. In this vein, a diethylamino group possesses greater vibrational degrees of freedom than does a morpholino group, for instance, which increases the probability of energy degradation or loss via radiationless transition channels from the Si state. This factor also explains the increased fluorescence quantum yields observed in the absence of one of the N-alkyl groups (cf. compounds II-V and VI, VII). Fixing the dialkylamino group in a ring, as in the transition from compounds VI and IX, for example, to coumarins XVIII and XIX also leads to enhanced fluorescence (Table 1).

In order to settle any remaining questions or controversy concerning the nature and degree of electronic influence of the amino groups in 4,7-dialkylaminocoumarins we have measured the pK$_{a}$ values of the conjugate acids of compounds I, III, IV, VI, IX, XII, XIII, XVI, XVII, and XIX (Table 2). Acidification of aqueous ethanol solutions of these coumarins is accompanied by a decrease in the position of and finally, by complete disappearance of their long-wavelength absorption maxima at...