

Intramolecular deactivation of substituted quinolinium cations. Time-resolved fluorescence and semi-empirical calculations

H. Lanig, M. Hof, T. Stahl, F.W. Schneider *

Institute of Physical Chemistry, University of Würzburg, Marcusstraße 9/11, D-97070 Würzburg, Germany

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Abstract

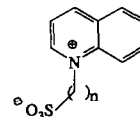
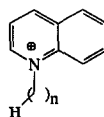
The fluorescence quenching of N-alkylated quinolinium ions with and without a sulfonato group at the chain end is investigated by measurement of their fluorescence lifetimes. The presence of the sulfonato group leads to a reduction of the fluorescence lifetime from 21.78 ± 0.12 ns for N-ethylquinolinium cation to 0.31 ± 0.05 ns for the sulfonatoethyl compound in CH_3CN . The high intramolecular quenching efficiency depends on the alkyl chain length in CH_3CN . However, in H_2O as solvent, there is no preferential quenching of fluorescence by the sulfonato group, which is strongly solvated. Semi-empirical calculations of sulfonatoalkylquinolinium betaines support the proposal of intramolecular ring formation as the cause of the strong quenching effects. The chain-length dependence of the fluorescence decay in CH_3CN is correlated with the different orientations of an interacting oxygen lone pair with the aromatic π system.

1. Introduction

As known from previous studies, the aromatic body of the betaines, the N-alkylquinolinium cation shows intermolecular excited-state adduct formation with large inorganic anions such as ClO_4^- and PF_6^- [1]. In the case of the corresponding betaines (B ($n=2-4$)) a SO_3^- group is attached to the end of the flexible alkyl chain (Fig. 1). If an energetically favourable interaction between the cationic aromate and the sulfonato anion exists, a cyclic conformation is expected to be stabilized. Assuming that intramolecular complex formation in the excited and/or ground state can be detected by fluorescence decay time measurements, the dynamic properties of different alkyl chains should influence the decay times.

In the present work, a number of betaines with various alkyl chain lengths (B ($n=2-4$)) have been syn-

thesized (Fig. 1) and their fluorescence decay times as well as the corresponding non-sulfonated compounds (A ($n=2-4$)) were measured in H_2O and CH_3CN . The dramatic differences in the lifetimes of the betaines and the N-alkylquinolinium cations support intramolecular complex formation. The effect of the conformations on the fluorescence lifetimes may



Compound Class A

n=2	1-(2-ethyl)quinolinium
n=3	1-(3-propyl)quinolinium
n=4	1-(4-butyl)quinolinium

Compound Class B

n=2	1-(2-sulfonatoethyl)quinolinium
n=3	1-(3-sulfonatopropyl)quinolinium
n=4	1-(4-sulfonatobutyl)quinolinium

Fig. 1. 1-(n-alkyl)quinolinium cations and 1-(n-sulfonatoalkyl)quinolinium betaines with different chain lengths.

* Corresponding author.

be interpreted on the basis of semi-empirical calculations.

2. Methods

2.1. Measurement of the decay times

A time-correlated single-photon counting technique (Edinburgh Instruments, model 199S) using simultaneous acquisition of fluorescence and excitation (SAFE) [2] was employed to determine the fluorescence decay times. The excitation and emission wavelengths were 337 and 420 nm, respectively, for all measured compounds. The data were analyzed using a conventional iterative convolution technique as described elsewhere [3]. Each reported decay time is the average of ten measurements with low values of χ^2 (< 1.2). The given experimental apparatus allows precise measurements of lifetimes with standard deviations of less than 1%. Absorption and fluorescence spectra were recorded on a Hitachi U3210 VIS/UV spectrometer and an American Instrument Co. SP500 fluorescence spectrometer, respectively.

2.2. Synthesis

The compounds 1-(2-sulfonatoethyl)quinolinium (B($n=2$)), 1-(3-sulfonatopropyl)quinolinium (B($n=3$)) and 1-(4-sulfonatobutyl)quinolinium (B($n=4$)) were synthesized according to standard procedures [4] with occasional modifications. They were purified by HPLC and characterized by $^1\text{H-NMR}$, IR spectroscopy and differential scanning calorimetry.

2.3. Computational procedures

In order to determine the geometries and resulting energy values of molecular conformations, a combination of molecular mechanics and semi-empirical methods was used. To search the potential energy surface of the given structures, the Monte Carlo type routine RIPS (random incremental pulse search) [5] was used in combination with Allinger's MM2 force field [6]. The resulting conformations found in the RIPS searches were refined and analyzed by MNDO-PM3 [7], implemented in the molecular orbital

package VAMP 4.5 [8], by the use of the energy-optimized output from the MM2 calculations as an input for the semi-empirical calculations.

3. Results and discussion

3.1. Fluorescence decay of N-alkylquinolinium cations and betaines

In order to investigate the dynamics of the intramolecular interaction between the aromatic body and the sidechain (R-SO_3^-), the fluorescence decay times of the compounds 1-(2-sulfonatoethyl)quinolinium, 1-(3-sulfonatopropyl)quinolinium and 1-(4-sulfonatobutyl)quinolinium (compound class B) were measured at 298 K (Table 1) and compared with the lifetimes of the corresponding non-sulfonated derivatives (compound class A) in H_2O and CH_3CN .

The lifetimes in H_2O are about 14 ns and are only weakly dependent on the structure of the sidechain. In marked contrast the lifetimes of class A compounds in CH_3CN are ≈ 22 ns whereas those of class B in CH_3CN are substantially shorter. In addition, the sulfonated compounds show a significant dependence on the chain length of the sulfonatoalkyl group, where the lifetime is shortest for $n=2$ (0.31 ± 0.05 ns) in CH_3CN . Fig. 2 shows decay curves and the

Table 1
Fluorescence lifetimes τ_f (ns) of N-alkylquinolinium hexafluorophosphates and N-sulfonatoalkylquinolinium betaines in CH_3CN and H_2O . The concentrations are 1×10^{-5} M for each compound, the temperature 298 K

n	Decay times in H_2O (ns)	
	class A	class B
2	14.33 ± 0.11	14.24 ± 0.14
3	14.32 ± 0.12	13.19 ± 0.13
4	14.40 ± 0.08	14.18 ± 0.18
n	Decay times in CH_3CN (ns)	
	class A	class B
2	21.68 ± 0.12	0.31 ± 0.05
3	21.69 ± 0.10	1.21 ± 0.02
4	21.77 ± 0.15	1.02 ± 0.02

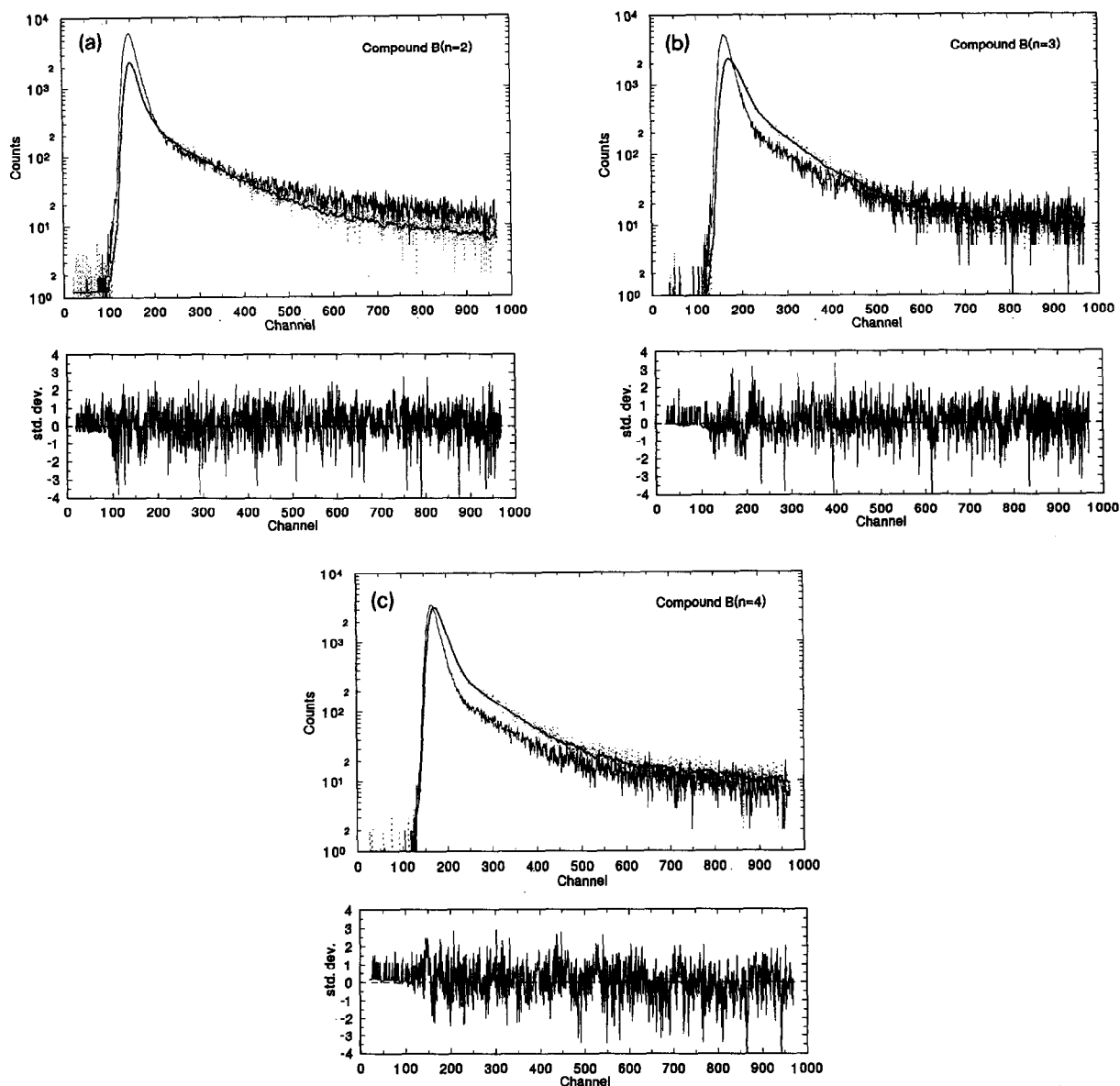


Fig. 2. Fluorescence decay curves and weighted residual plots of the compounds (a) $B(n=2)$, (b) $B(n=3)$ and (c) $B(n=4)$ recorded at 298 K. Each plot shows the lamp pulse (solid line), and probe pulse (dots) and the monoexponential fit curve (thick line).

corresponding residual plots for each compound ($B(n=2-4)$) to show monoexponential behaviour. The lifetimes of the alkylquinolinium ions without ionic end group are independent of chain length within experimental error in both solvents.

The absorption spectra of all compounds are practically identical concerning shape and location of the

bands. Therefore, an intramolecular complex in the ground state is not likely to exist, or, if it exists, it affects ground- and excited-state energy levels equally. Nevertheless, charge-transfer bands may be weak or covered by other bands. Since the fluorescence properties do not change within several days, any photochemical reaction can be excluded. The lifetimes and

stationary spectra do not show any dependence on dye concentration (1×10^{-5} to 1×10^{-2} M), excluding any intermolecular complex formation.

We conclude from the lifetime measurements that the solvation of these compounds in H_2O is effective and consequently intramolecular interactions between the aromatic ring and the sidechain are less important in H_2O than in CH_3CN . CH_3CN seems to interact only weakly with these ions. This hypothesis is supported by their very low solubility in CH_3CN . The lifetimes of alkylated quinolinium cations in CH_3CN are around 22 ns, due to inefficient CH_3CN quenching. They do not depend on the length of the alkyl group. Therefore, a significant contribution of vibrational or rotational motions of the alkyl chain to the quenching process can be excluded.

Attaching a sulfonato group to the alkyl chain (compound class B) shortens the lifetimes dramatically in CH_3CN (0.31 ± 0.05 ns for $n=2$) compared with 21.68 ± 0.12 ns for $A(n=2)$. This indicates a strong interaction between the cationic aromatic ring and the anionic sulfonato group in CH_3CN . A possible interpretation of the observed behaviour is the formation of a non-fluorescent excited-state complex, possibly accompanied by partial charge transfer. Therefore, intramolecular interactions may be responsible for the dramatic increase in the radiationless transition rates in CH_3CN .

To test the hypothesis of intramolecular fluorescence quenching, the decay times for the compounds $A(n=2)$ and $B(n=2-4)$ were measured in CH_3CN over a temperature range from 230 to 298 K (Fig. 3). All decay times are strictly monoexponential ($\chi^2 < 1.2$).

Compound $A(n=2)$ shows a slight increase in the fluorescence decay time upon cooling. This behaviour is probably caused by decreasing solvent–chromophore interaction (quenching). $B(n=2)$ reveals only a weak temperature dependence. In this case, intramolecular complex formation is very efficient and determines the fluorescence behaviour due to strong internal quenching. The enhanced temperature sensitivity of the compounds $B(n=3, 4)$ may be caused by the longer and more flexible alkyl spacers between the interacting fragments, which restrict the ability of intramolecular complex formation. The fluorescence decay times for $B(n=3, 4)$ in CH_3CN (Fig. 3) tend to reach values of ≈ 14 ns for $B(n=2-4)$ in H_2O

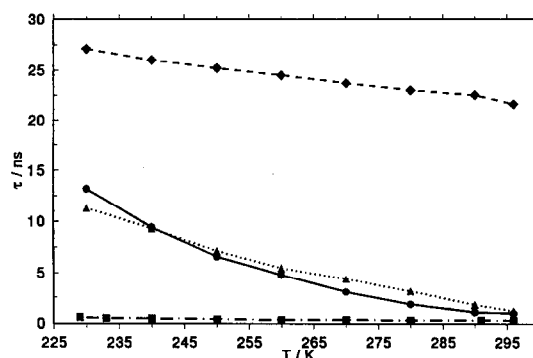


Fig. 3. Temperature dependence of the fluorescence decay times of the compounds $A(n=2)$ and $B(n=2-4)$ in CH_3CN . No change in the phase of the solvent occurs in the displayed temperature range. (---) $A(n=2)$, (—) $B(n=4)$, (···) $B(n=3)$, (-·-·) $B(n=2)$.

(Table 1). Upon cooling, the dielectric constant ϵ of CH_3CN increases from 36.7 (298 K) to 47.7 (229 K) [9]. This polarity enhancement of CH_3CN increases the solvation of the zwitterionic charges and weakens their Coulomb interaction comparable to the situation in water.

3.2. Semi-empirical calculations

A requirement for the proposed intramolecular complex formation is a sufficiently small distance between the interacting groups and an optimal overlap of the involved orbitals. The resulting cyclic conformations must be energetically favoured. It is well known that the ground-state conformation influences the formation of complexes in the excited state [10]. Therefore, the following calculations will only consider ground-state geometries.

In order to explain the lifetime dependence on the chain length, the conformational energy surface of each molecule was probed by the random incremental pulse search technique [5]. The energy-optimized MM2 [6] geometries served as starting points for a subsequent minimization using the PM3 Hamiltonian [7]. The standard enthalpies of formation (H_f^0 , 298 K) of the most significant conformations were calculated (Table 2). A detailed description of these procedures will be given [11].

The results of these calculations are:

– Compound class A: The enthalpies of formation

Table 2

Standard enthalpies of formation H_f° , percent contributions (according to Boltzmann statistics) and angles ϕ between the plane of the aromatic ring and the closest S–O bond (Fig. 5) of the three most favourable conformations for each compound in class B

Compound	H_f° (kcal/mol)	%	ϕ (deg) ^a
$n=2$	-40.29	99.90	0.3
	-35.94	0.06	
	-33.74	0.02	
$n=3$	-48.35	99.30	21.0
	-45.40	0.35	
	-45.09	0.28	
$n=4$	-56.59	99.10	9.4
	-53.56	0.59	
	-53.35	0.30	

^a The angle ϕ is given only for the most favourable conformation of each compound.

for all conformations were found to be constant within 0.1 kcal/mol. Therefore no preferred conformations for the unsulfonated molecules exist and any stable conformation of the side chain is equally probable.

– Compound class B: The calculations show that a cyclic structure of the side chain is most favourable. For example, for 1-(2-sulfonatoethyl)quinolinium the enthalpy of formation of the noncyclic conformation is about 20 kcal/mol higher than the enthalpy of the cyclic conformation. The set of enthalpies for the most favourable conformations of all three compounds are given in Table 2. These conformations show a short distance (0.28 nm) between the α -carbon ring atom and the closest oxygen atom of the sulfonato group (Fig. 4). Since this distance is equal for all three minima (B($n=2-4$)), the lifetime dependence on the chain length may be caused by different orientations of the interacting groups.

In order to explain the chain-length dependence of the sulfonatoalkylquinolinium betaines, the angle ϕ between the aromatic ring plane (π system) and the closest sulfur–oxygen bond was calculated (Table 2). The smallest angle (0.3°) was found for B($n=2$) indicating that the interaction is optimal for this chain length. This is reasonable since the p_z orbital of the oxygen atom overlaps optimally with the π orbitals of the ring (for $n=2$).

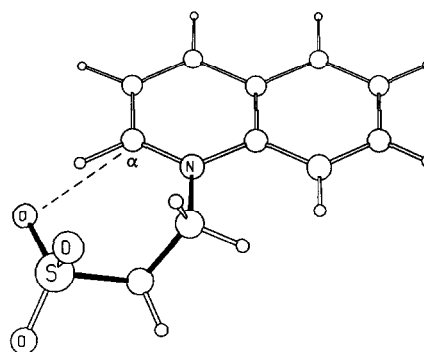


Fig. 4. Most favourable conformation of the compound B($n=2$), where ring formation of the sidechain with the α -carbon atom of the aromatic ring is shown by darkened bonds.

It should be mentioned that the calculations do not include any solvent effects. Therefore, they may be used only for the interpretation of the measured decay times in weakly interacting solvents (with low solubility) such as CH_3CN rather than in highly polar solvents such as H_2O , in which polar and ionic groups are strongly solvated.

3.3. Intramolecular quenching processes of sulfonatoalkylquinolinium betaines

Semi-empirical calculations of the geometries show that an attractive interaction between the α -carbon of the aromatic system and an oxygen atom of the sulfonato group exists. This leads to energetically favoured cyclic structures.

We speculate that in an electronically excited quinolinium betaine the attractive interaction between the α -carbon and the oxygen atom may lead to the formation of a non-fluorescent intramolecular complex. The orientation of the interacting orbitals (π system of the excited aromatic ring and a nonbonding p_z orbital of the nearest oxygen atom) determines the stability of the intramolecular complex [11] and therefore the fluorescence quenching efficiency (Fig. 5). Our calculations show that the angle ϕ between the nearest S–O bond and the plane of the aromatic ring is 0.3° for the ethyl compound. Thus an optical overlap of the interacting orbitals is achieved in the compound yielding the lowest fluorescence lifetime ($\tau_f = 0.31 \pm 0.05$ ns). Assuming that a small angle between the interacting orbitals leads to the most stable

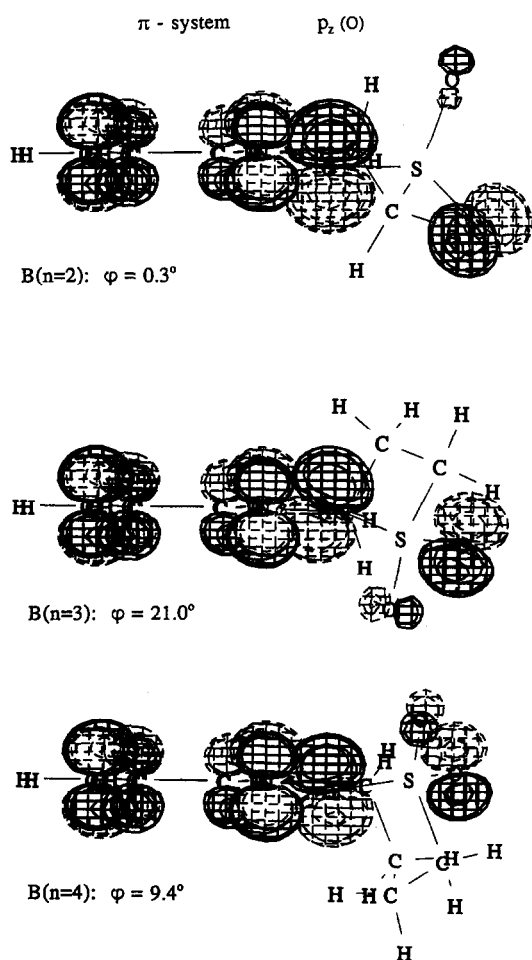


Fig. 5. Most favourable conformations of the compounds B ($n=2-4$). The chosen perspective shows the orientation of the interacting p_z -lone pair of one oxygen atom and the aromatic π system. φ is the angle between the plane defined by the aromatic body and the closest S–O bond. The axes of the p_z orbitals are represented by dashed lines.

complex the values for the propyl $\varphi=21.0^\circ$ ($\tau_f=1.21 \pm 0.02$ ns) and butyl $\varphi=9.4^\circ$ ($\tau_f=1.02 \pm 0.02$ ns) derivatives (Tables 1 and 2) are in good agreement with the observed trend in the fluorescence lifetimes.

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