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Theoretical investigation of the effect of the solvent, hydrogen bond and amino group on the isomerization of Rhodamines

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ABSTRACT

The isomerization between two forms of Rhodamine dyes, namely the lactone and zwitterion, have been investigated theoretically in solution phase at the B3LYP/6-31 + G(d,p) level of theory with the polarizable continuum model (PCM). The isomerization energy barrier between the lactone and zwitterion of Rhodamine 110 in solvents of different polarity is calculated. The solvent polarity has little effect on the isomerization energy barrier of Rhodamine 110, though a linear correlation between the energy barrier and solvent polarity is found. The effect of the hydrogen bonds at five sites of Rhodamine 110 on the energy barrier of isomerization is investigated by the inclusion of an explicit methanol molecule in addition to the PCM approach. The energy barrier of Rhodamine dyes with different amino groups is calculated at the PCM-B3LYP/6-31 + G(d,p) level of theory to clarify the role of the amino groups in the isomerization of Rhodamines. The change of the energy barrier is explained by the electrostatic repulsion between the xanthene ring and the carboxyl group as evidenced by the linear relation between the energy barrier of the isomerization and the lactonic C–O distance under different conditions. The relative energies of lactone and zwitterion, which are affected by solvent, hydrogen bonds and the amino groups, are also discussed.

1. Introduction

The photophysical properties of Rhodamines have been extensively studied since these compounds are widely used as laser dyes [1], fluorescent probes [2], sensitizers in dye sensitized solar cells [3], and chemosensors in detection of small molecules [4]. The molecular structure of Rhodamines is characterized by a xanthene ring substituted by two amino groups and an *ortho*-carboxyphenyl at the 9-position carbon. The *ortho*-carboxyphenyl is roughly perpendicular to the xanthene skeleton as shown in Fig. 1. In solution Rhodamines exist in the lactone and zwitterion forms (Fig. 2) [5–8]. The zwitterion form only exists in protic solvents and is absent in aprotic solvents, whereas the lactone form can exist in both protic and aprotic solvents.

The equilibrium between the lactone and zwitterion forms depends on the solvent polarity and hydrogen bond interaction [5–8]. A good relationship between ln *K* (*K* is the equilibrium constant) and the solvent dielectric constant is found in alcohols [7], which indicates that the equilibrium shifts to the zwitterion from the lactone as the solvent polarity increases. Theoretical calculations of the tetramethyl-rhodamine [9] and tetramethyl-rhodamine isothiocyanate [10,11] also confirm that the zwitterion form is more stable than the lactone in the solvents of high polarity.

The hydrogen bond, which occurs at the charged COO^- group of the zwitterion form, could stabilize solute dipole and negative charge of the COO^- group and contribute to a tendency to favor the zwitterion relative to the lactone. This result has been demonstrated by both the experimental observations [6–7] and theoretical calculations [9,10]. Furthermore, the hydrogen bond between the amino groups of Rhodamines and solvent could affect the photophysics of Rhodamines [12–14].

The amino groups of the xanthene moiety of Rhodamine dyes can lead to severe changes of the photophysical properties [2,14–17]. The alkylation of the amino groups can lead to the important decreases in the fluorescence lifetimes and quantum yields and the increase of the nonradiative rate constants from the first excited state to the ground state [16,17]. In several recent studies, the substituent has been considered as an important factor which has influence on the tautomeric equilibrium and relative stability of different isomers [18–22]. However, to the best of our knowledge, none of the previous published studies was dedicated to the effect of the amino groups on the equilibrium of the zwitterion and lactone.

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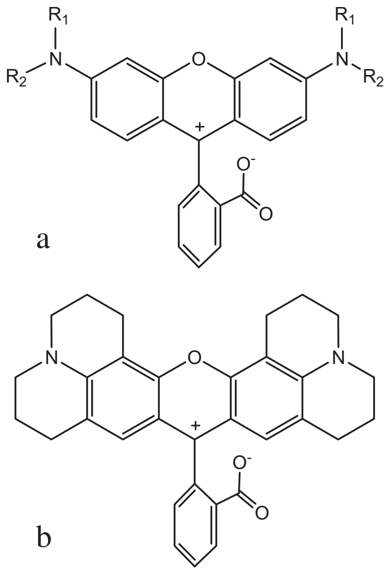

Fig. 1. Molecular structures of Rhodamines in the zwitterion form studied here. (a) Rhodamine 110: $R_1 = R_2 = H$; TetramethylRhodamine: $R_1 = R_2 = CH_3$; Rhodamine B: $R_1 = R_2 = C_2H_5$. (b) Rhodamine 101.

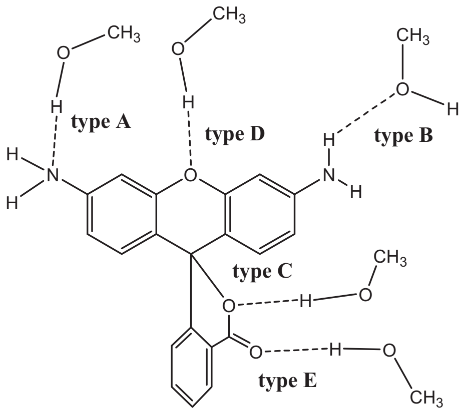

Fig. 3. Illustration of different types of hydrogen bonds between Rhodamine 110 and methanol.

In the present work we have carried out a series of theoretical calculations to investigate the isomerization of Rhodamine 110 in different solvents. We focus on the energy barrier of the isomerization and the relative energies of two forms and how these properties are affected by solvent, hydrogen bonds at different sites. The polarizable continuum model (PCM), which replaces the microscopic description of the solvent by a polarizable dielectric medium, is used to consider the bulk solvent effect. When hydrogen bonds between the solvent and the solute may exist, the so-called discrete/PCM approach has been used. In this approach a small number of solvent molecules are treated with full quantum calculations and the rest is treated with the PCM. Recent studies have found that the discrete/PCM approach is a powerful tool for treating the relative stability of different isomers and the hydrogen bond effect in solution phase [18–21]. In the present work, the PCM and the discrete/PCM approaches are used. Five specific sites of Rhodamine 110 are possible to form hydrogen bonds, which include the participation of the amino nitrogen (type A), amino hydrogen (type B), xanthene oxygen (type D) and two carbonyl oxygens (type C and E) of Rhodamine 110 with a solvent molecule as illustrated in Fig. 3. Knowledge of the hydrogen bond interaction enables a better understanding of how the local environment of the chromophore modulates the isomerization and the photophysics of Rhodamines. Furthermore, theoretical calculations of Rhodamine 101, Rhodamine B and tetramethylRhodamine, which are different by the amino groups as shown in Fig. 1, are also carried out to shed light on the effect of the amino group on the energy barrier of the isomerization and the relative energies of the lactone and zwitterion.

2. Computational methods

All calculations were carried out using the Gaussian 09 program package [23]. The geometry optimizations in solution were performed at the B3LYP level of theory [24–26] with the 6-31 + G(d,p) basis sets [27–31]. Harmonic vibrational frequencies were calculated at the same level to validate whether the obtained structure was a minimum (all frequencies are real) or a transition state (only one imaginary frequency). The intrinsic reaction coordinate (IRC) calculations were also carried out to confirm the connection between the transition state and the minima. Further calculations are performed using B3LYP/6-31 + G(d,p) with the D3 version of Grimme's dispersion corrections [32] to see the dispersion effect.

In this work the solvent effect was mandatory for all calculations using the polarizable continuum model (PCM) of Tomasi [33]. Alternatively, the discrete/PCM approach was used to investigate the effect of hydrogen bonds on the energy barrier of the isomerization and the relative energy of two forms by inserting an explicit solvent molecule in the first solvation shell at different sites of Rhodamine 110.

Natural population and natural bond orbital (NBO) analysis [34] were performed with the NBO program at the B3LYP/6-31 + G(d,p) level of theory. This method allows one to analyze hydrogen bond as an $n \rightarrow \sigma^*$ charge transfer interaction. The charge transfer not only results in an increase in hydrogen bond energy but also allows the monomers to approach each other very closely [34]. The importance of this interaction can be evaluated by the second-

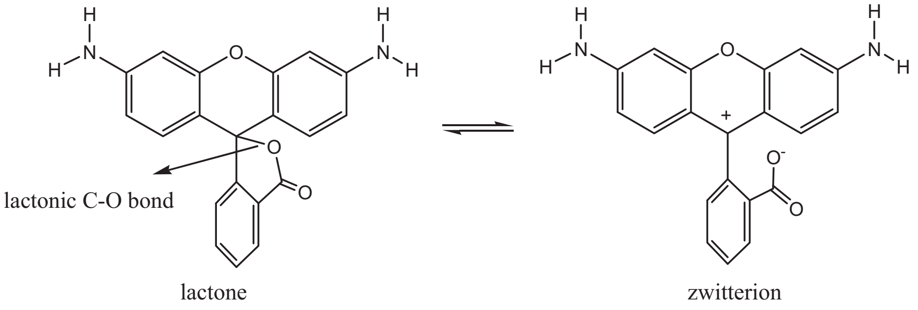

Fig. 2. Molecular structures of the lactone (left) and zwitterions (right) of Rhodamine 110 and the equilibrium between two forms is presented.