

COMMUNICATION

Effects of Different-type Intermolecular Hydrogen Bonds on the Geometrical and Spectral Properties of 6-aminocoumarin Clusters in Solution

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Received 18 June 2013; Accepted (in revised version) 10 July 2013

Abstract: Geometrical and spectral properties of the hydrogen-bonded clusters formed by 6-aminocoumarin (6AC) with solvents of different hydrogen-bonding abilities have been investigated at CPCM-PBE0/6-311++G(d, p) theory level. Upon photo-excitation, type hydrogen bonds will be weakened whereas hydrogen bonds of B and C types should be strengthened. The weakening of hydrogen bond A is responsible for the blue-shifts of the absorption spectra in HFIP and TFE while strengthening of hydrogen bonds B₁ and B₂ are reasons for the red-shifts of the absorption spectra in DMSO. The absorption spectra of cluster 6AC-(H₂O)₃ is in better agreement with the experimental result than 6AC-(H₂O)₅.

AMS subject classifications: 74E40, 78M50

Keywords: 6-aminocoumarin clusters Hydrogen bonds of different types, Hydrogen bonding strengthening and weakening, Spectral red- and blue-shifts.

1. Introduction

Recently, important results on many properties of intermolecular hydrogen bonds, including their structures, energy changes upon electronic excitation as well as their impacts on the

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spectral and photophysical properties of hydrogen-bonded chromophore molecules can be found in a number of theoretical [1-12] and experimental [13-24] works. Some TDDFT calculations have been performed to examine the relationship between the absorption spectra of 7-aminocoumarin and the formation of hydrogen bonds [3-5]. Using DFT and TDDFT methods, Zhao and Han [6] have demonstrated that the strengthening of the intermolecular hydrogen bonds upon photoexcitation can lower the excitation energy of a related excited state and induce an electronic spectral redshift, while the excited-state hydrogen bond weakening can heighten the excitation energy of a related excited state and induce an electronic spectral blueshift. Moreover, hydrogen bond formation and its effects on the absorption and fluorescence spectra of coumarins molecules are also the subjects of experimental works [14-17].

Krystkowiak and coworkers [25-26] have measured the absorption spectra of 6-aminocoumarin (6AC) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), 2,2,2-trifluoroethanol (TFE), dimethylsulfoxide (DMSO) and water and compared with those in 1-chloro-*n*-propane (1-C₃H₇Cl). They concluded that the unusual blue- and red-shifts of absorption spectra of 6AC in solvents HFIP (TFE) and DMSO should be due to the weakening of hydrogen bond N...H-O (A type) and strengthening of hydrogen bonds N-H...O (C type) as a result of the excitation. In addition, they suggested the solute-solvent complexes made by all possible hydrogen bonds, that is 6AC-(HFIP)₃, 6AC-(TFE)₃, 6AC-(DMSO)₂ and 6AC-(H₂O)₅. However, as pointed out by Krystkowiak in the Introduction of Ref. 26, only theoretical calculations permit determinations of the geometrical structures of the hydrogen-bonded clusters and energies of the individual hydrogen bond formed in the clusters.

Table 1: The Kamlet and Taft (K-T)

parameters (α, β) and the dielectric constant ϵ of the solvents.

Solvent	α	β	ϵ
1-C ₃ H ₇ Cl	0.00	0.00	8.59
HFIP	1.97	0.00	16.62
TFE	1.51	0.00	26.67
DMSO	0.00	0.76	46.45
H ₂ O	1.17	0.47	78.00

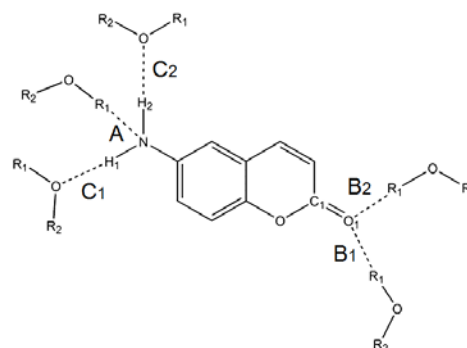


Figure 1: Illustration of three types of intermolecular hydrogen bonds formed between 6-aminocoumarin (6AC) and solvents.

6AC shows a simple structure as the 1,2-benzopyrone moiety is substituted by donor