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Absorption, fluorescence, and semiempirical ASED-MO studies on a typical Brooker's merocyanine dye

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Abstract

Solvatochromism and Solvatofluorchromism of Brooker's merocyanine 1-methyl-4- (4′-hydroxystyryl) pyridinium betaine, M, were studied in twelve polar protic and aprotic solvents. Moderate hypsochromic fluorescence energy shifts are 4.57 kcal mole^{-1} while strong hypsochromic absorption energy shifts are 16.63 kcal mole^{-1}. Decreasing of the dipole moment of M upon excitation is the factor, which is responsible for the difference between the two energy shifts. The change of both energies rectilinearly with solvent acidity scale shows the importance of oxygen atom of M as a strong basic center. The application of the atom superposition and electron delocalization molecular orbital (ASED-MO) theory reproduces geometrical and electronic structures for M, which agree well with the experimental observations. The calculations suggest strongly that the dye has a benzenoid valence structure in the ground state and shifts towards a quinonoid one upon excitation with an observed decreasing of the dipole moment. The changing of the dipole moment is explained clearly depending upon the calculated charge distribution over the whole skeleton of the molecule. The formation of a H-bond between the water molecule and the highly negative oxycyclic oxygen atom of M has slightly effect on its dipole moment in the ground state. This leads to suggest that this kind of interaction could be represented as attacking of water with acidic character on the basic site of M. Also, the calculations predict that the formation of monohydrated complex is an exothermic, down hill reaction, which is confirmed from the stabilization of the frontier molecular orbitals, oxygen lone-pair and the HOMO levels.

Keywords: Merocyanine; Solvatochromism; Solvatofluorchromism; ASED-MO calculations

1. Introduction

Merocyanines of stilbazolium betaine have been found interesting owing to their extreme solvatochromic properties.[1–11] The sensitivity of the absorption spectra of these compounds to medium effects permits their use as sensitive probes of solvent polarity. Extensive experimental studies [12–18] of merocyanine (M) have been continued. The molecular structure of M has electron donor and acceptor centers at the terminals of the structure offering two mesomeric structures, the benzenoid form M_b and the quinonoid form M_q as a result of the intramolecular charge transfer.

The valence structure of the conjugated π-electron system should be altered to have probably the intermediate polymethine form, M_{pm}, (Scheme 1) which has an equal contribution from both mesomeric structures M_b and M_q of certain ground and excited state energies. [19] The concept of an ideal polymethine state (IPS) is introduced by Dähne. [20] For the IPS, the π-electron density distribution along the polymethine chain is of maximum alternation and the π bond orders level off, in the ground state as well as in an excited state. Theoretical studies of a typical Brooker's cyanine dye showed well consistent with the structure given by Dähne's conception of IPS. [21,22]

Jacques [14] and Abdel-Halim et al. [15] have studied the solvatochromism of M with different polar solvents in the ground state which is characterized by its extreme hypsochromic shifts. This behavior was attributed to the decreasing of its dipole moment upon excitation. The dipole moment increases with increasing of solvent polarity in the ground state.

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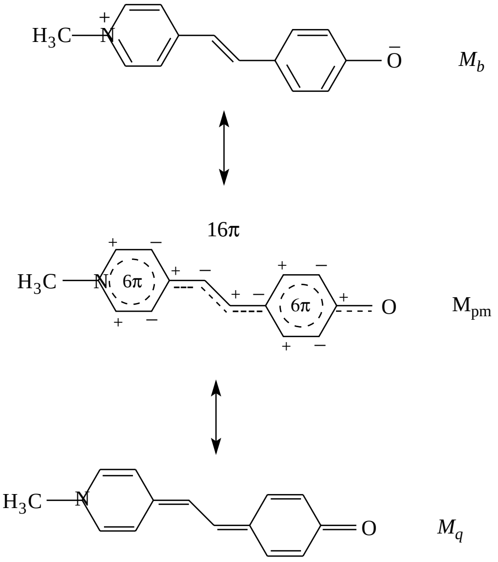

Scheme 1.

It has found a good correlation between a solvatokinetic thermal cis/ trans isomerization of M and its solvatochromism. [15] Recently, El-Sayed et al. [23] carried out femtoseconds transient absorption experiments in water solvent. They found that the photoexcitation of M leads to a conformer intermediate M* with a time constant of 1.1 ps and decays with a time of 5.8 ps back to the ground state.

The crystal structure analysis has been done to investigate the planarity and the zwitterionic character of the compound. [24] It is shown that the simple merocyanine M is essentially planar in the solid state and exists as the benzenoid structure. Also, it has been suggested that the hydrogen bonds are formed between the carbonyl end of the molecule and the hydrogen atom of water solvent molecules. [24] Meanwhile, hydrogen bonds are presented to exist between the molecules of solvent. Investigation of the structure of merocyanine M has been carried out using considerable number of spectroscopic and quantum chemical studies including semiempirical and ab initio calculations. [25–38] Some of the data obtained from different theoretical studies could be criticized because its calculations could not correctly reproduce the optimized molecular structure in the gas phase which correlate well with the crystallographic X-ray data, see Table 1. Besides, they have just calculated the values of the dipole moments without explaining the correlation between the actual

Table 1
The calculated gas phase bond lengths (Å) of merocyanine from different methods versus crystallographic data

Bond length	PM3[a]	AM1[a]	DFT[a]	ASED-MO		X-ray[b] data
				Ground	Excited	
O1–C2	1.223	1.242	1.261	1.29	1.27	1.304
C2–C3	1.478	1.471	1.481	1.43	1.41	1.421
C3–C4	1.342	1.347	1.372	1.37	1.36	1.370
C4–C5	1.452	1.449	1.454	1.39	1.40	1.404
C5–C6	1.453	1.454	1.455	1.38	1.40	1.408
C6–C7	1.342	1.346	1.373	1.37	1.37	1.379
C2–C7	1.478	1.469	1.477	1.41	1.43	1.414
C5–C8	1.360	1.364	1.411	1.44	1.39	1.439
C8–C9	1.432	1.425	1.417	1.34	1.42	1.346
C9–C10	1.363	1.366	1.409	1.43	1.40	1.441
C10–C11	1.447	1.446	1.458	1.35	1.39	1.405
C11–C12	1.354	1.365	1.372	1.40	1.37	1.359
C12–N13	1.406	1.388	1.393	1.38	1.38	1.353
N13–C15	1.406	1.388	1.395	1.34	1.38	1.347
C10–C14	1.448	1.450	1.455	1.39	1.40	1.407
C14–C15	1.355	1.364	1.371	1.38	1.37	1.361
N13–C16	1.473	1.436	1.478	1.49	1.48	1.479

[a] Data obtained from Ref. [38], Parametric model 3 (PM3), Austin model 1 (AM1) and Density function theory (DFT).
[b] Ref. [24].