

Mechanism of Water Attacking on Brooker's Merocyanine Dye and Its Effect on the Molecular and Electronic Structures: Theoretical Study

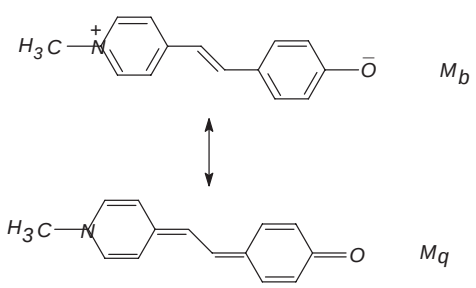
Mohamed K. Awad* **and Shakir T. Abdel-Halim**

Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

Received August 11, 2005; E-mail: Mkhawad@hotmail.com

Semiempirical molecular orbital calculations have been performed to study the mechanism by which water molecules attack the highly negative oxycyclic oxygen atom of Brooker's merocyanine 1-methyl-4-(4′-oxidostyryl)pyridinium betaine, M, to form mono-, di-, and tri-hydrated merocyanine complexes. In the case of mono- and di-hydrated complexes, one or two water molecules attack the oxygen atom, respectively, but in the case of the tri-hydrated complex, only two water molecules attack the oxygen atom of M with sp^2 hybridization, while the third one forms a H-bond with either one of the oxygen atoms of the coordinated water molecules. The effect of H-bond formation on the molecular and electronic structures of merocyanine is investigated using the atom superposition and electron delocalization molecular orbital (ASED-MO) theory. The calculations show that the hydrated complexes are shifted towards the benzenoid valence structures in the ground state, but shifted towards quinonoid ones upon excitation. On the basis of the calculated charge distribution over the whole skeleton of the complexes, it is found that the dipole moments of the complexes are slightly affected by H-bond formation in the ground state, but strongly decrease upon excitation. The formation of hydrated merocyanine complexes are highly exothermic, downhill reactions, which is explained with respect to the stabilization of the HOMO and oxygen lone-pair levels. We believe that the attacking by water with acidic character on the basic site oxygen atom of merocyanine is a kind of acid–base interaction.

Brooker's merocyanine dye, M, has been found to be of interest owing to its extreme solvatochromic and solvatofluorochromic properties in different polar solvents.[1–11] It was found in our previous study that moderate hypsochromic fluorescence energy shifts are 4.57 kcal mol^{-1}, while strong hypsochromic absorption energy shifts are 16.63 kcal mol^{-1}. The strong energetic stabilization in water as a solvent is probably due to the small size of the water molecule, which creates a compact solvation depending on both its high ability of dipolarity/polarizability and strong hydrogen-bond formation. Different experimental and theoretical studies have strongly suggested that one of the main factors contributing to the solvatochromic shifts is the formation of a hydrogen bond between the oxygen atom of merocyanine and the solvent.[2,7,12–19] 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 (Scheme 1). Stable hydrogen-bonded structures have been predicted to be formed.



Scheme 1.

The predominant contribution of the benzenoid structure has a highly relative dipole moment that is suitable for the dipole/dipole interactions. Also, it has a phenoxide oxygen atom exhibiting a highly basic electron-pair donor center, which is suitable for specific hydrogen-bonding interaction. The stability of the ground and excited states increases with increasing the acidity character of the solvent.[12] As reported previously, the results of the elemental analysis and H_2O determination with a Mitsubishi moisture meter showed that the crystal water content corresponded to $3H_2O$ molecules for M.[19] Crystal structure analysis has been done to investigate the planarity and the zwitterionic character of the compound.[20] It is shown that the simple merocyanine M is essentially planar in the solid state and exists as the trihydrate benzenoid structure. The H atom positions are partially located and calculated on the basis of geometrical studies. The positions of the hydrogen atoms in the intermolecular H-bonds are not usually very accurate by X-ray analysis.[20] Meanwhile, hydrogen bonds are presented to exist between the molecules of the solvent. It has been concluded from ^1H and ^{13}C NMR studies that the corrected structure of M in solutions resembles strongly the zwitterion structure and the observed hypsochromic shift arises primarily from the H-bonding interaction between merocyanine oxygen atoms and protic solvents such as water and formamide.[15] Investigation of the structure of merocyanine M has been carried out using a considerable number of spectroscopic and quantum chemical studies including semiempirical and ab initio calculations.[3,7,16,17,21–25] The ASED-MO calculations have been applied[12,26,27] to investigate the formation of H-bonded complexes, and gave a good prediction to the expected molecular structures of H-bonded complexes.

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In the present work, the ASED-MO method is performed to investigate the mechanism of attacking by water molecules on the oxycyclic oxygen atom of M to form mono-, di-, and trihydrated merocyanine complexes through the H-bond formation, which comes from the full optimization of bond lengths, bond angles, and dihedral angles of the hydrated complexes. The geometries of these complexes are confirmed with ab initio calculations. Also, the effect of the formation of H-bonding on the electronic and molecular structures of merocyanine is investigated by calculating the charge distribution over the whole skeleton of the molecule and its correlation with the changing of dipole moments is explained. Moreover, the effect of the formation of H-bonds on the energies of molecular orbitals of hydrated complexes is also studied to explain the hypsochromic shifts of these complexes.

Theoretical Methods

The ASED-MO technique is a semiempirical approach based on a partitioning of molecular electronic density functions into atomic and delocalization components.[28,29] Using the electrostatic theorem, the forces on the nuclei are integrated as the atoms are brought into a molecular configuration to yield a repulsive energy due to rigid atom densities and an attractive energy due to electron delocalization. The sum is the exact molecular binding energy. In the ASED-MO method, the atom superposition energy (E_R) is calculated from the actual atomic densities, whereas the electron delocalization attractive energy is approximated as the change in the total one-electron valence orbital energy (ΔE_{MO}) obtained by using a modified extended Hückel–Hamiltonian:

$$E = E_R + \Delta E_{MO}. \quad (1)$$

This technique is used to predict molecular structures, stabilities, electronic properties, and reaction pathways (see Refs. 30–34). The input data consist of valence state Slater orbital exponents[35] and experimental valence state ionization potentials (VSIP)[36] for the constituent atoms. These parameters are sometimes altered (particularly in treating ionic heteronuclear molecules) to ensure reasonably accurate calculations of ionicities and bond lengths in diatomic fragment molecules. In this way, electronic charge self-consistency is taken into account.[29] The diatomic parameters are used in studying larger molecules. The atomic parameters used in the calculations are given in Table 1. Because of ionicity, the ionization potentials for N 2s and 2p are decreased by 2.5 eV from the atomic values.[36] Also, Slater exponents for N 2s and 2p are decreased by 0.30 au from the atomic values of Clementi and Raimondi[35] to get a reasonable bond length. Unshifted parameters are used for C, O, and H, Table 1. In all calculations the C–H bond lengths are kept constant at 1.10 Å.

Table 1. Atomic Parameters Used in the Calculations: Principle Quantum Numbers, n; Ionization Potentials, IP (eV); Orbital Exponents, ζ (au)

Atom	s			p		
	n	IP	ζ	n	IP	ζ
C	2	16.590	1.6580	2	11.260	1.6180
N	2	17.830	1.6237	2	12.040	1.6170
O	2	28.480	2.2459	2	13.620	2.2266
H	1	13.600	1.2000			

Also, ab initio calculations were carried out at the B3LYP/6-31+G* level using the Gaussian 98 suite of programs[37] to confirm the geometry of the attacked water molecules on the oxycyclic oxygen atom of M.

Results and Discussion

The application of the ASED-MO method was performed to study the geometrical and electronic structures of Brooker's merocyanine,[12] which shows agreement with the experimental observations.[20] It is shown that M has a benzenoid valence structure in the ground state, Fig. 1, shifting towards a quinonoid one upon excitation while changing from single–double–single character for the bridging polymethine chain to double–single–double character. The formation of a H-bond between a water molecule and the oxygen atom of M in the ground state shifts the merocyanine towards the zwitterion structure. Also, the calculations show that the dipole moment of M decreases upon excitation, while it is slightly increased upon formation of a H-bonded complex in the ground state. Also, the linear correlation of absorption and fluorescence energies, which has been obtained experimentally with respect to solvent acidity scale, shows that the stability of the ground and excited states increases with increasing the acidity character of the solvent.[12] This leads us to predict correctly that the attacking by water molecules on the highly negative oxygen atom of M could be considered as a kind of acid–base interaction.

Effect of Hydrogen Bond on the Molecular Structures. Let us start by explaining the formation of the mono-hydrated complex II. The calculated structure of complex II with the optimized bond lengths, bond angles, and dihedral angles is shown in Fig. 2. The calculations show a stable planar structure with a minimum energy when the dihedral angle is equal to zero. According to the following equation:

$$M + H_2O \rightarrow M\cdots H\text{–}O\text{–}H. \quad (2)$$

The ASED-MO calculations show that the formation of the H-bonded complex II is downhill by 0.877 eV, which is con-

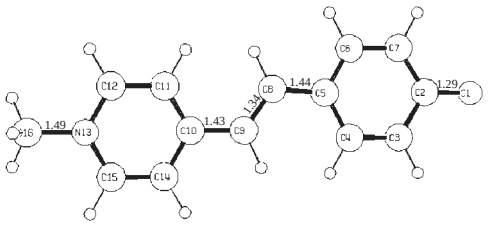

Fig. 1. Optimized geometrical structure of Brooker's merocyanine.

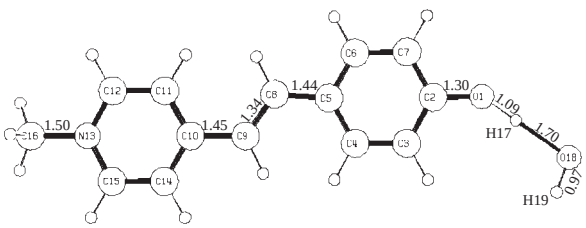

Fig. 2. Optimized geometrical structure of mono-hydrated merocyanine complex II.

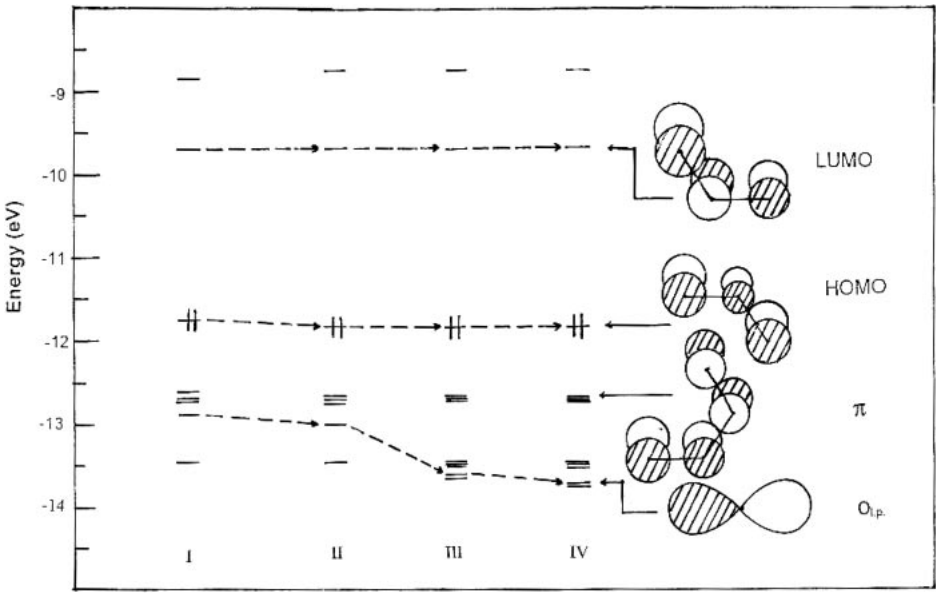

Fig. 3. Correlation diagram of the calculated electronic structures for the investigated compounds.

firmed from ab initio calculations with a quite close downhill, 0.632 eV. This means that attacking the oxygen atom of M leads to a great stabilizing effect. This can be seen also from the stabilization of the O_1 lone-pair orbital and the HOMO level by 0.149 and 0.028 eV, respectively (with respect to that in the case of M), and destabilization of the LUMO level by 0.022 eV, involving an increase of energy separations, ΔE, by 0.171 and 0.050 eV, respectively, Fig. 3 and Tables 5 and 6. The calculations show that complex II exists as a benzenoid structure with a C_2–O_1 bond length of 1.30 Å, which lies between the C=O double-bond length of around 1.22 Å found in *p*-benzoquinone[38] and the C–O single-bond length of around 1.33 Å found in hydrated sodium phenoxide.[39] Also, the corresponding C_5–C_8 and C_9–C_{10} bonds show single-bond character with bond lengths 1.44 and 1.45 Å, respectively, while the central C_8–C_9 bond shows double-bond character with a bond length equals to 1.34 Å. This is confirmed with the calculations of bond order between the atoms of the hydrated merocyanine II, Table 2. The calculations show a stronger central bond C_8–C_9, which has a bond-order value of 1.1123, than that in the case of M, 1.1063, and weaker C_5–C_8 and C_9–C_{10} bonds of 0.8338 and 0.8181, respectively. The approaching of a solvated water molecule to the oxygen atom weakens the C_2–O_1 bond to 0.7876 with respect to 0.8673 in the case of M. From this, it may be confirmed that complex II has a more zwitterionic character than that of M. The presence of the intermolecular hydrogen bond leads to small changes on the overall geometry of the M with an O_1–H_{17}–O_{18} distance of 2.79 Å. The calculations show the angle of H_{17}–O_1–C_2 equals 144°, and bond lengths O_1–H_{17} and H_{17}–O_{18} are equal to 1.09 and 1.70 Å, respectively. The hydrogen bond is almost linear with the O_1–H_{17}–O_{18} angle equal to 179°, while the H_{17}–O_{18}–H_{19} angle equals 105°. This data confirms our suggestion that the attacking by water molecules on merocyanine is an acid–base interaction, which agrees with the experimental observations. A similar optimized planar geometry for the attacking water molecule is obtained using ab initio calculations, which show O_1–H_{17}–O_{18} and H_{17}–O_{18}–H_{19} angles equal to 177 and 105°, respectively. Also, it is shown that the O_1–H_{17}–O_{18} distance equals 2.72 Å, with a long O_1–H_{17}, 1.71 Å, and short H_{17}–O_{18} bond, 1.01 Å. These differences are probably due to the different parameters used for semiempirical and ab initio methods. It is shown from the semiempirical and ab initio calculations that the bonded hydrogen O_{18}–H_{19} bond has a bond length equal to 0.97 Å.

Upon excitation, the structure of complex II shifts more towards the quinonoid structure. This is shown from the increasing double-bond character for C_2–O_1, C_5–C_8, C_9–C_{10}, and N_{13}–C_{16} bonds, from bond-order values, 0.8427, 0.9377, 0.9471, and 0.6677, respectively, in the case of the M* molecule, and to 0.8582, 0.9612, 0.9658, and 0.6873, respectively, in the case of hydrated complex II. Also, increasing the single-bond character of the C_8–C_9 bond from bond-order value 0.8862, in the case of M*, to 0.8899, in the case of complex II, has been calculated. This confirms that the formation of the H-bond in the excited state shifts the hydrated complexes towards the quinonoid structures.

It has been stated that there are two water molecules intermolecularly hydrogen bonded to the oxygen atom of M.[13] Therefore, we used the ASED-MO calculations to show clearly how two water molecules could interact with the merocyanine and investigate the effect of the formation of the H-bond on geometrical and electronic structures of M. In the monohydrated complex II, there are two negatively charged centers, O_1 and O_{18} atoms, with net charges −0.4998e and −1.2819e, respectively, Table 3, which could be considered as two basic centers available for forming H-bonds with the second molecule of water. Accordingly, there are two different possibilities for forming the di-hydrated complex III. The first one represents the attacking of a H atom of the second water molecule on the O_1 atom with sp^2 hybridization and the second one, representing a linear chain, is the formation of a H-bond between a H atom of the second water molecule and the O_{18} atom. The calculations obtained from the full optimization of both struc-

Table 2. The Calculated Bond Lengths (Å) and (Bond Orders) of Merocyanine and Its Hydrated Complexes in Ground State versus Crystallographic Data

Bond	Merocyanine (I)		Monohydrated (II)		Dihydrated (III)		Trihydrated (IV)		X-ray data
O1–C2	1.29	(0.8673)	1.30	(0.7876)	1.30	(0.7738)	1.31	(0.7620)	1.304
C2–C3	1.43	(0.8890)	1.40	(0.9332)	1.39	(0.9563)	1.39	(0.9551)	1.421
C3–C4	1.37	(1.0144)	1.36	(1.0174)	1.36	(1.0122)	1.35	(1.0243)	1.370
C4–C5	1.39	(0.9559)	1.38	(0.9691)	1.37	(0.9812)	1.37	(0.9784)	1.404
C5–C6	1.38	(0.9699)	1.38	(0.9766)	1.38	(0.9758)	1.38	(0.9777)	1.408
C6–C7	1.37	(1.0039)	1.39	(0.9855)	1.39	(0.9777)	1.39	(0.9755)	1.379
C2–C7	1.41	(0.9195)	1.38	(0.9654)	1.39	(0.9612)	1.39	(0.9698)	1.414
C5–C8	1.44	(0.8485)	1.44	(0.8338)	1.44	(0.8319)	1.44	(0.8322)	1.439
C8–C9	1.34	(1.1063)	1.34	(1.1123)	1.34	(1.1133)	1.34	(1.1132)	1.346
C9–C10	1.43	(0.8377)	1.45	(0.8181)	1.45	(0.8178)	1.45	(0.8179)	1.441
C10–C11	1.35	(1.0121)	1.37	(0.9894)	1.37	(0.9895)	1.37	(0.9895)	1.405
C11–C12	1.40	(0.9613)	1.38	(0.9809)	1.38	(0.9808)	1.38	(0.9808)	1.359
C12–N13	1.38	(0.9569)	1.36	(0.9792)	1.36	(0.9792)	1.36	(0.9792)	1.353
N13–C15	1.34	(0.9957)	1.36	(0.9783)	1.36	(0.9784)	1.36	(0.9783)	1.347
C10–C14	1.39	(0.9591)	1.38	(9.9762)	1.38	(0.9763)	1.38	(0.9763)	1.407
C14–C15	1.38	(0.9842)	1.38	(0.9833)	1.38	(0.9832)	1.38	(0.9833)	1.361
N13–C16	1.49	(0.6742)	1.50	(0.6663)	1.50	(0.6663)	1.50	(0.6663)	1.479
O1–H17	—	—	1.09	(0.5752)	1.08	(0.6925)	0.97	(0.6897)	
H17–O18	—	—	1.70	(0.0545)	1.92	(0.0177)	1.97	(0.0108)	
O18–H19	—	—	0.97	(0.6686)	0.97	(0.6662)	0.96	(0.6839)	
O1–H20	—	—	—		1.05	(0.6634)	0.99	(0.6696)	
H20–O21	—	—	—		1.78	(0.0156)	1.91	(0.0198)	
O21–H22	—	—	—		0.97	(0.6661)	0.97	(0.6667)	
O18–H23	—	—	—		—		0.97	(0.6670)	
H23–O24	—	—	—		—		1.86	(0.0224)	
O24–H25	—	—	—		—		0.97	(0.6667)	

tures show that a stable structure is formed in the first case with a downhill of 1.452 eV. The obtained optimized molecular structure of the di-hydrated complex III is shown in Fig. 4. The calculations suggest that complex III is planar and exists mainly as the benzenoid valence structure with a C_2–O_1 bond length 1.30 Å, which agrees with the experimental observations.[20] The two attached water molecules form intermolecular H-bonds with O_1–O_{18} and O_1–O_{21} distances of 3.0 and 2.83 Å, respectively. The calculated O_1–H_{17} and O_1–H_{20} bond lengths, 1.08 and 1.05 Å (1.71 and 1.01 Å from the ab initio method), respectively, are almost linear with O_1–H_{17}–O_{18} and O_1–H_{20}–O_{21} angles of 185 and 184° (with respect to 182° obtained from ab initio calculations), respectively. The angles within the hydrated water molecules H_{17}–O_{18}–H_{19} and H_{20}–O_{21}–H_{22} are 132 and 133°, respectively, which is similar to that obtained from the ab initio calculation, 128°, with respect to 105° in the case of a free water molecule. It is shown from the calculations that the binding of two water molecules to M leads to more benzenoid structures in the ground state and, accordingly, to more quinonoid structures in the excited state, Table 2. The calculated Mulliken overlap populations show that the C_2–O_1 bond becomes weaker on binding to two water molecules, with the bond-order value 0.7738, than that in the case of M, 0.8673. Also, C_5–C_8 and C_9–C_{10} bonds get weaker with bond-order values equal to 0.8319 and 0.8178, respectively, while the C_8–C_9 bond becomes stronger, with a value of 1.1133, than those in the case of M, which agrees with the suggestion of the presence of the zwitterion structure for the di-hydrated complex III.

Table 3. The Calculated Net Charge on Each Atom of M and Its Hydrated Complexes in the Ground State Obtained from the ASED-MO Method

Atom	Merocyanine	Monohydrated	Dihydrated	Trihydrated
O1	−1.1643	−0.4998	0.2521	0.3150
C2	0.5091	0.4634	0.4173	0.4133
C3	−0.0934	−0.0819	−0.0668	−0.0639
C4	0.0298	0.0325	0.0327	0.0345
C5	−0.0421	−0.0396	−0.0313	−0.0330
C6	0.0349	0.0296	0.0270	0.0265
C7	−0.0959	−0.0912	−0.0833	−0.0848
C8	0.0364	0.0380	0.0373	0.0373
C9	−0.0331	−0.0360	−0.0328	−0.0336
C10	0.0807	0.0773	0.0774	0.0774
C11	0.0008	0.0002	0.0007	0.0006
C12	0.1950	0.1993	0.1993	0.1993
N13	0.4796	0.4758	0.4763	0.4762
C14	−0.0018	0.0043	0.0048	0.0047
C15	0.1972	0.1983	0.1983	−0.1983
C16	0.1669	0.1663	0.1663	0.1663
H17	—	0.3001	0.2622	0.2626
O18	—	−1.2819	−1.2975	−0.6044
H19	—	0.3460	0.3452	0.2969
H20	—	—	0.2655	0.2618
O21	—	—	−1.2957	−1.3212
H22	—	—	0.3459	0.3471
H23	—	—	—	0.2978
O24	—	—	—	−1.3206
H25	—	—	—	0.3469

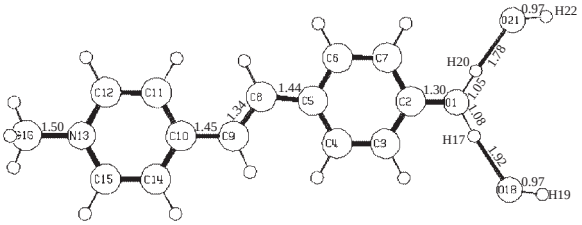

Fig. 4. Optimized geometrical structure of di-hydrated merocyanine complex III.

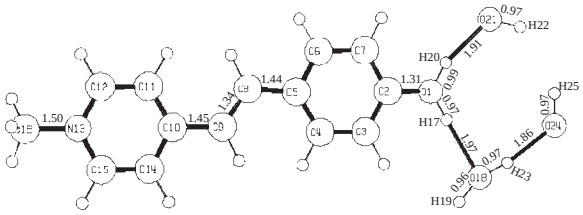

Fig. 5. Optimized geometrical structure of tri-hydrated merocyanine complex IV.

To our knowledge, there is not enough information explaining how three molecules of water could bind to the merocyanine; therefore, we used the ASED-MO method to investigate the mechanism of formation of the tri-hydrated complex IV. Accordingly, it is suggested that there are three different possibilities to form complex IV: 1) $2H_2O$ molecules attack the O_1 atom to form the di-hydrated complex III. The calculations of charge distribution over the whole of molecule III show a large decrease in charge density on the O_1 atom from -1.1643e, in the case of M to 0.2521e. Accordingly, the possibility of attacking by the third water molecule on the O_1 atom of M is excluded, while the O_{18} and O_{21} atoms of water molecules still have high charge densities, -1.2975e and -1.2957e, respectively, representing two basic sites, which could facilitate the attacking of a H atom of water to form H-bonds. The third molecule attacks either O_{18} or O_{21} atoms by two pathways: i) It forms a H-bond with either one of them while the second H atom gets to the other O atom with a distance of 2.868 Å, which means that $3H_2O$ molecules surround the O_1 atom of M. ii) Donating one H atom to the O_{18} or O_{21} atom to form as an example the O_{18}–H_{23} bond while it forms a H-bond with the H_{22} atom of the second water molecule to form the O_{24}–H_{22} bond. It is shown from the calculations that the first pathway is downhill 2.099 eV, while the second pathway is downhill 1.689 eV. 2) $3H_2O$ molecules attack the O_1 atom of M as sp^3, which gives an unstable complex uphill 4.121 eV, which leads us to exclude it. This is in contradiction with the suggestion by other different studies.[16,17] 3) $3H_2O$ molecules could be represented as a chain attacking the O_1 atom of M to form a H-bond. The end of the chain could move and get closer to the O_1 atom with a calculated distance equal to 3.1 Å, which shows a downhill of 0.341 eV. According to the above mechanisms, it seems that the preferred molecular structure for the tri-hydrated complex IV is coming from the first pathway of the first possibility, as shown in Fig. 5. The calculations show that the tri-hydrated complex IV is planar and exists as a zwitterion valence structure with the C_2–O_1 bond slightly stretched to be 1.31 Å, which agrees with the X-ray data, Table 2. The C_5–C_8 and C_9–C_{10} bonds show single-bond character with bond lengths 1.44 and 1.45 Å, respectively, while a double-bond character is shown for the C_8–C_9 bond of 1.34 Å. The approaching of the third molecule of water strengthens the H-bonding between the oxygen atom of merocyanine and the H atom of the attached water molecules with O_1–O_{18} and O_1–O_{21} bond lengths equal to 2.94 and 2.90 Å (with respect to 2.78 Å using the ab initio method), respectively. The O_1–H_{17} and O_1–H_{20} bonds have similar bond lengths compared with the ab initio method, 0.97 and 0.99 Å, respectively, with O_1–H_{17}–O_{18} and O_1–H_{20}–O_{21} angles equal to 180 and 197° (compared with 178° from ab initio calculations), respectively. The calculations show that the O_{18}–O_{24} bond length equals 2.83 Å, while it is 2.78 Å in the case of the ab initio method. The O_{18}–H_{23} bond length is 0.97 Å with the O_{18}–H_{23}–O_{24} angle equal to 170° with respect to 174° in the case of the ab initio method. The angles H_{19}–O_{18}–H_{17}, H_{22}–O_{21}–H_{20}, and H_{25}–O_{24}–H_{23} have values equal to 109, 123, and 128°, respectively, compared with 128° from the ab initio method. The presence of highly negative charged O_{21} and O_{24} atoms of the tri-hydrated complex, Table 3, could form additional H-bonds with further water molecules to give a complex such as a hexa-hydrated molecule, which agrees with the suggestion of the X-ray data.[20] The calculated Mulliken overlap population confirms the benzenoid valence structure for the hydrated merocyanine complexes, Table 2.

Effect of H-Bond on the Electronic Structure of Merocyanine. The calculated charge distribution over the whole skeleton of the molecule obtained from the ASED-MO method, could explain the mechanism for attacking by the water molecules on the O_1 atom of M, and also shows the dependence of the change of the dipole moment on the changing of charges. The calculations show that the high charge density on the O_1 atom, -1.1643e, favors the water to attack and form the hydrated complex II, which decreases the charge density to be -0.4998e and electron deficiency on the C_2 atom from 0.5091e to 0.4634e, Table 3. Also, the charge on the O_{18} atom is increased to -1.2819e and is less electron deficient on the bonded H_{17} atom, 0.3001e, in respect to -0.6148e and 0.3074e, in the case of a free water molecule, respectively. Meanwhile, an increase in the electron deficiency of the non-bonded H_{19} atom from 0.3074e to 0.3460e is calculated on binding to M. Accordingly, the charge on the negative end of the hydrated phenoxy moiety is slightly increased to -0.9304e with respect to -0.9282e in the case of the phenoxy moiety of M due to the formation of a H-bond. On the other hand, the calculations show that the charge on the positive end, pyridinium moiety, is slightly increased from 0.9683e to 0.9711e. The polymethine chain has a charge equal to -0.0414e compared with -0.0402e in the case of M. Attacking of M by a water molecule in the ground state has a slight effect on the charge distribution, Table 4. The above data confirms that formation of complex II is a kind of acidic character interaction of water with the highly negative charged oxygen atom as a basic site of M, which agrees with the experimental observations.[12]

Upon excitation of complex II, the dipole moment decreases due to the decrease of positive and negative charges on the N_{13} and O_1 atoms, from 0.4758e and -0.4998e to 0.3976e and

Table 4. The Calculated Charges on Different Moieties of M and Hydrated Complexes in the Ground and Excited States

Group	Merocyanine I		Complex II		Complex III		Complex IV	
	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited
Hydrated phenoxy[a)]	−0.9282	−0.5699	−0.9304	−0.5714	−0.9339	−0.5740	−0.9327	−0.5770
Pyridinium	0.9683	0.7441	0.9711	0.7491	0.9727	0.7521	0.9724	0.7562
Polymethine chain	−0.0402	−0.1740	−0.0414	−0.1775	−0.0389	−0.1783	−0.0397	−0.1793

a) Phenoxy moiety attached with water molecules except for merocyanine I.

Table 5. The Energies of the Frontier Orbitals and the Separation Energy, ΔE (eV), and Type of Transition Obtained from the ASED-MO Theory

Compound	E_{HOMO}	E_{LUMO}	ΔE (nm)	Transition
Merocyanine (I)	−11.748	−9.708	2.040 (607)	$\pi \rightarrow \pi^*$
Monohydrated (II)	−11.776	−9.686	2.090 (593)	$\pi \rightarrow \pi^*$
Dihydrated (III)	−11.801	−9.689	2.112 (587)	$\pi \rightarrow \pi^*$
Trihydrated (IV)	−11.802	−9.687	2.115 (586)	$\pi \rightarrow \pi^*$

Table 6. The Energies of the Oxygen Lone-Pair and Frontier Orbitals and the Separation Energy, ΔE (eV), and Type of Transition Obtained from the ASED-MO Theory

Compound	$O_{l.p.}$	LUMO	ΔE (nm)	Transition
Merocyanine (I)	−12.871	−9.708	3.163 (392)	$n \rightarrow \pi^*$
Monohydrated (II)	−13.020	−9.686	3.334 (372)	$n \rightarrow \pi^*$
Dihydrated (III)	−13.620	−9.689	3.931 (315)	$n \rightarrow \pi^*$
Trihydrated (IV)	−13.703	−9.687	4.016 (309)	$n \rightarrow \pi^*$

−0.3899e, respectively. This can also be shown from the calculations of the decreasing of both positive and negative charges on pyridinium and hydrated phenoxy moieties to 0.7491e and −0.5714e, respectively, and the increasing of the negative charge on the polymethine chain to −0.1775e, Table 4. Meanwhile, a decrease in negative charge on the O_1–H_{17}–O_{18}–H_{19} moiety from −1.1356e to −1.0078e is calculated upon excitation. It is shown from Table 4 that the formation of hydrated complexes II, III, and IV in the excited state leads to a slight increase in their dipole moments, which confirms that the attacking by water molecules on M is a kind of acid–base interaction. This is also confirmed from the application of the ASED-MO method to investigate the nature of electronic transitions and calculate their energies for hydrated merocyanine complexes.

It has been expected that the electronic spectra of the complexes are dominated by the π–π^* transitions.[16–18] To see how the ASED-MO theory could explain the electronic structures with their excitation energies, Figure 3 shows the calculated orbital energies and structures of compounds I, II, III, and IV. The attacking of water molecules to form H-bonded complexes leads to stabilization of the HOMO level of the hydrated complexes II, III, and IV by 0.028, 0.053, and 0.054 eV, and destabilization of the LUMO level by 0.022, 0.019, and 0.021 eV, respectively, with respect to that in the case of M. This increases the separation energies, ΔE, between the HOMO–LUMO levels to be 2.090, 2.112, and 2.115 eV, respectively, compared with 2.040 eV, in the case of M, Table 5. The changes of energy show that there is an increase in the stability of the hydrated merocyanine complexes as a result of increasing the acidity character effect, which is due to the increasing of the interaction of binding water molecules with M. The formation of a H-bond could further polarize the molecule to increase the stabilization of orbitals and produce higher excitation energies. This is also confirmed from the ab initio calculations, which also show an increasing of HOMO–LUMO gaps, 5.485, 5.690, 5.732, and 5.754 for compounds I, II, III, and IV, respectively. These lowest transition energies correspond to $\pi \rightarrow \pi^*$ transitions that are mainly described by one electron excitation from the HOMO levels, characterized by coefficients of considerable greater amplitude on the O_1, C_2, C_8, and C_9 atoms, to the LUMO levels with complete π^* character with greater coefficients on the C_8 and C_9 atoms. Also, the attacking by water molecules leads to a difference in excitation energies between the HOMO–LUMO levels ranging from 607–586 nm (about 22 nm), which explains how the effect of the formation of the H-bond is a kind of hypsochromic shift property. Other $\pi \rightarrow \pi^*$ transitions are calculated with an excitation energy for complexes of about 2.979 eV, which corresponds to a transition from the next HOMO orbital with greater contribution from the C_8 and C_9 atoms to the π^* orbital. This is in a good agreement with the experimental excitation energy, 2.799 eV.[12,40] Another evidence for the stability of hydrated complexes is shown from the higher stabilization of oxygen lone-pair orbitals of the hydrated complexes by about 0.149, 0.749, and 0.832 eV, respectively, with respect to that in the case of M, Table 6. This stabilization could explain the increase in the basic character of the oxygen atom of M. The calculations indicate excitations with energies 3.334, 3.931, and 4.016 eV, respectively, corresponding to $n \rightarrow \pi^*$ transitions that are mainly described by an electron excitation from the oxygen lone-pairs orbitals to the LUMO orbital with complete π^* character.

Conclusion

The mechanism of attacking by water molecules on the highly negative oxycyclic oxygen atom of Brooker's merocyanine M to form hydrated complexes through the formation of H-bonds has been investigated using the ASED-MO method. It is shown from the calculations that the hydrated complexes are planar and have benzenoid valence structures in the ground state, but shift towards the quinonoid structures upon excitation, which agrees with the experimental observations. Studying the charge distribution over the whole skeleton using semiempirical molecular orbital calculations could confirm the mechanism of water attacking the oxygen atom of M. The calculations show decreasing charge density of the oxygen atom from −1.1643e, in the case of M to −0.4998e, 0.2521e, and 0.3150e in the cases of mono-, di-, and tri-hydrated complexes, respectively. In the case of the formation of mono- and

di-hydrated complexes, only two water molecules attack the oxygen atom of M; while the third one can not attack the highly electron deficient oxygen atom, it attacks either one of the two oxygen atoms of bonded water molecules to form a H-bond, which is in contradiction with that suggested by other studies. The geometry of the attacked water molecules to M is also confirmed using ab initio calculations. The differences of charge distribution over the whole skeleton for the hydrated complexes lead to a slight increase in their dipoles with small changes on the overall geometry of M. Upon excitation, the dipole moment of the hydrated complexes is strongly decreased as in the case of M. Also, the stabilization of π-bonding and non-bonding oxygen lone-pair orbitals could explain the hypsochromic shift for the hydrated complexes. These results confirm our suggestion that the attacking by water molecules of the highly negative oxygen atom of M is a kind of acid–base interaction.

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