

Solvent Effects on the Bond Length Alternation and Absorption Energy of Conjugated Compounds

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Solvent effects have profound influence on the structure and electronic properties of organic materials with extended π -conjugations.^{1–3} The idea of tuning solute geometry with varying solvent polarity to yield desired optical properties has been a long-sought-after goal in materials research.^{4,5} Recent experimental studies by Marder and co-workers have demonstrated the importance of solvent effects on the geometry and nonlinear optical properties of conjugated organic molecules.^{1,6} The extent of geometric distortion induced by solvent or an external electric field can be characterized by bond-length alternation (BLA),^{5a} defined as the average difference in length between single and double bonds in the conjugated pathway. Because of its relevance to the rational design of molecules with large hyperpolarizabilities, it is of great interest to develop computational strategies to provide insight into the solvent effect on BLA and optical properties of conjugated compounds.^{3,7–9} In this paper, we present a Monte Carlo (MC) simulation study of the solvent effect on BLA and electronic absorption energy of two merocyanine compounds, 3-aminopropenal (**I**) and 5-(dimethylamino)pentadienal (**II**), in solution. The method can easily be extended to the study of structural and solvent effects on hyperpolarizabilities of organic molecules.^{3,9}

We make use of a hybrid quantum mechanical and molecular mechanical (QM/MM) technique that has been developed for the study of solvatochromic shifts of chromophores in solution through MC simulations.^{10,11} In this approach, the solute molecule is treated by a configuration interaction (CI) wave function in the presence of explicit solvent molecules. The latter is approximated by an MM force field.^{12–14} To determine the

BLA of conjugated molecules in solution at 25 °C, the bond lengths and bond angles of the solute molecule are varied and averaged along with solvent configurations using standard Metropolis sampling throughout the simulation. The maximum bond length and angle variations for each solute move are ± 0.015 Å and $\pm 0.5^\circ$, which yield an average solute acceptance rate of about 50%. This allows thermal fluctuations and the effect of solvent configurations to be included in the averaging.

The average Franck–Condon excitation energy of the solute in solution ($\langle \Delta E_{\text{tot}}^{\text{g} \rightarrow \text{e}} \rangle$), is determined by two contributing factors: the static solvent energy $\Delta E_{\text{Cl}}^{\text{g} \rightarrow \text{e}}$, which is evaluated using the ground state configuration and an effective pair potential for the solvent, and the energy contribution due to the instantaneous polarization of solvent molecules following the solute electronic excitation ($\Delta E_{\text{pol}}^{\text{g} \rightarrow \text{e}}$). To evaluate $\Delta E_{\text{pol}}^{\text{g} \rightarrow \text{e}}$, a polarizable solvent model must be used which accounts for the solvent charge redistribution upon the solute electronic excitation (eq 1):^{14,15}

$$\Delta E_{\text{pol}}^{\text{g} \rightarrow \text{e}} = \frac{1}{2} \sum_{\text{s}} [\mu_{\text{s}}^{\text{e}} \cdot E_{\text{s}}(\Phi_{\text{Cl}}^{\text{e}}) - \mu_{\text{s}}^{\text{g}} \cdot E_{\text{s}}(\Phi_{\text{Cl}}^{\text{g}})] - \frac{1}{2} \sum_{\text{s}} \Delta \mu_{\text{s}}^{\text{g} \rightarrow \text{e}} \cdot E_{\text{s}}^{\text{o}}(\text{MM}) - \sum_{\text{s}} \Delta \mu_{\text{s}}^{\text{g} \rightarrow \text{e}} \cdot E_{\text{s}}(\Phi_{\text{Cl}}^{\text{e}}) \quad (1)$$

In eq 1, $\mu_{\text{s}}^{\text{g}}$ and $\mu_{\text{s}}^{\text{e}}$ are solvent dipoles in the presence of the solute in its ground and excited state, and $\Delta \mu_{\text{s}}^{\text{g} \rightarrow \text{e}} = \mu_{\text{s}}^{\text{e}} - \mu_{\text{s}}^{\text{g}}$. $E_{\text{s}}(\Phi_{\text{Cl}}^{\text{g}})$, $E_{\text{s}}(\Phi_{\text{Cl}}^{\text{e}})$, and $E_{\text{s}}^{\text{o}}(\text{MM})$ are electric fields on solvent atoms resulting from the solute ground state, from the solute excited state wave function, and from all other solvent permanent charges. An iterative procedure described in refs 14 and 15 is used to obtain these quantities.

The computed average molecular geometries of chromophores **I** and **II** in various solvents are listed in Table 1. Standard errors are estimated from averages of 10^5 configuration blocks, which are less than 0.002 Å for all bond distances. Changes in bond lengths and bond angles are relatively small in comparison to the effect of external electric fields observed previously;³ however, the general pattern on BLA can still be demonstrated. In nonpolar solvent (CCl_4), the geometries of **I** and **II** are characterized by a polyenic structure, with a computed BLA of 0.091 ± 0.003 Å for **I** and 0.094 ± 0.003 Å for **II**, similar to those in the gas phase. As the solvent polarity increases, the BLA values decrease to 0.046 ± 0.003 and 0.058 ± 0.003 Å in water. This is in accord with a recent study using a continuum solvent model.³ In a series of experimental studies, Marder et al. showed that geometries and Raman spectra of simple donor/acceptor polyenes are strongly influenced by solvent polarity or crystalline environment.⁶ It was demonstrated that for $\text{R}_2\text{N}(\text{CH}=\text{CH})_n\text{CHO}$, where $n = 2$ or 3, the average difference between the carbon single bond and double bond is reduced from 0.11 Å in the gas phase to 0.05 Å in the crystalline state and in polar solvents. This experimental observation is in excellent agreement with our computational results for systems with $n = 1$ and 2 in water.

Computed ground state dipole moments are given in Table 1. The computed dipole moments for **I** and **II** are 5.5 and 6.7 D in the gas phase and CCl_4 , which may be compared with the

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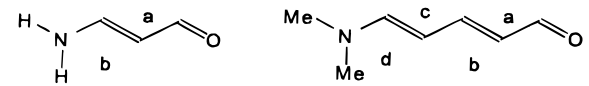
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Table 1. Computed Average Bond Lengths (Å) and Dipole Moments (D) of Chromophores **I** and **II** in Solution at 25 °C^a


solvent	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	ΔR	μ
Compound I						
vacuo	1.452	1.362			0.091	5.51
CCl ₄	1.453	1.362			0.091	5.55 ± 0.01
MeOMe	1.444	1.370			0.074	7.11 ± 0.04
MeCN	1.439	1.373			0.066	7.69 ± 0.07
MeOH	1.433	1.376			0.057	8.79 ± 0.09
H ₂ O	1.429	1.383			0.046	9.49 ± 0.10
Compound II						
vacuo	1.461	1.347	1.436	1.363	0.094	6.74 (7.62) ²⁰
CCl ₄	1.462	1.349	1.438	1.365	0.093	6.77 ± 0.03
MeOMe	1.456	1.350	1.432	1.368	0.085	8.42 ± 0.09
MeCN	1.458	1.351	1.426	1.370	0.082	8.85 ± 0.08
MeOH	1.455	1.348	1.432	1.371	0.084	9.06 ± 0.14
H ₂ O	1.438	1.363	1.421	1.381	0.058	12.87 ± 0.19

^a The semiempirical AM1 method is used to describe the solute in hybrid QM/MM MC simulations,¹⁶ with Jorgensen's TIP3P and OPLS potentials for the solvent.¹⁷ All simulations are executed in the NPT ensemble at 25 °C and 1 atm for one solute in a cubic box containing 500 water or 260 organic solvent molecules along with periodic boundary conditions and a spherical cutoff of 10 Å for aqueous and 12 Å for organic solvents. At least 1×10^6 configurations are used in the equilibration, followed by 1.5×10^6 configurations for data collection. Standard errors are about 0.002 Å.

experimental value for **II** (7.6 D).²⁰ However, the dipole moments are 7.7 and 8.8 D for **I** and **II** in acetonitrile and are further increased to 9.5 and 12.9 D, respectively, in aqueous solution, giving rise to induced dipoles of 4.0 and 6.2 D over the corresponding gas phase values. Clearly, as the chain length of the polyenic unit extends, the charge polarization leads to more extended charge separations and enhanced solvent effects on molecular dipole moments.

Solvent effects on the $\pi \rightarrow \pi^*$ transition for **II** are obtained in hybrid QM-CI/MM MC simulations. The computed solvatochromic shift, which is defined as the difference in maximum absorption energy in solution and in the gas phase ($\langle \Delta\nu(\text{tot}) \rangle = \langle \Delta E_{\text{tot}}^{\text{g} \rightarrow \text{e}} \rangle - \langle \Delta E_{\text{gas}}^{\text{g} \rightarrow \text{e}} \rangle$), can be separated into two contributing factors: the change of absorption energy due to BLA of the chromophore in solution, $\langle \Delta\nu(\text{stru}) \rangle$, and the differential solute-solvent interaction energy in the ground and excited state, $\langle \Delta\nu(\text{sol}) \rangle$. The gas phase absorption energy for the $\pi \rightarrow \pi^*$ transition of **II** is predicted to be 30 034 cm⁻¹, while the excitation energy is slightly red-shifted to 29 909 ± 50 cm⁻¹ in CCl₄ at 25 °C and 1 atm. The latter value is in good accord with the experimental result for **II** in hexane (30 170 cm⁻¹).²¹

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Table 2. Computed Solvatochromic Shifts (cm⁻¹) and Contributions from Structural Variation and Solvation Effects in Various Solvents at 25 °C^a

solvent	ϵ	$\langle \Delta\nu(\text{stru}) \rangle$	$\langle \Delta\nu(\text{sol}) \rangle$	$\langle \Delta\nu(\text{tot}) \rangle$	exptl
CCl ₄	2.2	-109	-16	-125 ± 48	
MeOMe	4.2	-260	-825	-1085 ± 89	
MeCN	35.9	-375	-1040	-1415 ± 72	
MeOH	32.5	-278	-1130	-1408 ± 113	
H ₂ O	78.2	-948	-1424	-2372 ± 89	-4030

^a Excitation energies are determined by CI single calculations for 10-electron/9-orbital "active space".¹⁸ In determining $\Delta E_{\text{pol}}^{\text{g} \rightarrow \text{e}}$, Dang's POL2 model is used for water using configurations saved during QM/MM simulations with the TIP3P model.¹⁹ Since there are no suitable polarizable potential functions for the organic systems, the polarization correction has been neglected for these solvents, which introduces errors of about 100–200 cm⁻¹ in the computed spectral shifts.¹⁵ For aqueous solution, the computed $\Delta E_{\text{pol}}^{\text{g} \rightarrow \text{e}}$ is -101 cm⁻¹. All spectral shifts are relative to the gas phase value. Negative signs indicate red-shifts (lower excitation energies). See also footnotes of Table 1.

The agreement provides support for the use of the semiempirical CIS method in the present study. As the solvent polarity increases, the chromophore structure becomes more distorted as indicated by the decreased BLA (Table 1). This structural variation is accompanied by a reduction in the energy gap between the ground and the excited state relative to that in the gas phase ($\langle \Delta\nu(\text{stru}) \rangle$). The computed red-shifts in the absorption energy due to BLA range from 109 cm⁻¹ in CCl₄ to 950 cm⁻¹ in water. Solvent effects further reduce the absorption energy and increase as the solvent polarity and hydrogen bonding abilities are enhanced. Table 2 reveals that the hydrogen bonding effect in water makes the most significant contribution. In water, the computed solvatochromic shift for the $\pi \rightarrow \pi^*$ transition of **II** is -2372 ± 90 cm⁻¹, which may be compared with the experimental spectra shift of -4030 cm⁻¹ going from hexane to water.^{5,21}

In summary, we have demonstrated that hybrid QM/MM simulation techniques may be used to determine solvent effects on the geometry of conjugated donor/acceptor molecules. The computed bond-length alternation from the gas phase to aqueous solution was found to be in accord with experiments. In addition, solvatochromic shifts of the $\pi \rightarrow \pi^*$ absorption energy for 5-(dimethylamino)pentadienal have been computed, and contributing components from structural variation and solvent effects were analyzed. Studies of geometrical and solvent effects on hyperpolarizabilities of conjugated molecules are in progress using such a hybrid QM/MM simulation method.

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