Protonation of Bipyridines and Their Vinylene−Phenylene−Vinylene Derivatives: Theoretical Analysis of the Positive Charge Effects

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Torsion analysis of the bipyridine (BPy) segment was carried out on the free and protonated bipyridines (head-to-head) as well as their vinylene−phenylene−vinylene (VPV) derivatives with semiempirical AM1 calculations to determine the configuration of protonated species. The hydrogen bonding energy has been estimated through comparison of the energy barriers with those of the free base form. Intramolecular hydrogen bonding plays an important role in the ring torsion where one nitrogen atom is protonated. Torsion potentials are prodominated by repulsion between the positive charges where both nitrogen atoms are protonated. Proton bonding to nitrogen has strong electron withdrawing effect. It stabilizes the HOMO and LUMO, with the second being the most affected. Consequently, protonation decreases the HOMO/LUMO energy gap. These protonation effects will be gradually reduced as the counterions come closer to the protons. The first transition energies were calculated with ZINDO/SCI methods and compared with the AM1 calculated HOMO/LUMO energy gaps at various torsion angles. The theoretical results support the ion-induced as well as protonation induced red-shifting of both the absorption and emission maximum of bipyridine contained polymers.

Introduction

Pyridine-based conducting polymers have received intense investigation due to their facile n-doping (reduction) and their ability to bind different guest species to the lone pairs of nitrogen atoms of the pyridine rings.[1−4] The effect of the protonation of bipyridine (BPy) contained polymers attracted particular interest. Monkman et al.[5] studied the protonation effects on the photophysical properties of poly(2,5-pyridine diyl) and found that the photoluminescence quantum yield (PLQY) in the solid state and the observed shifts between solution and solid-state emission wavelength can be described using a simple ring torsion argument. Eichen et al.[6] studied the effect of protonation−deprotonation processes on the electrooptical properties of bipyridine-containing poly(*p*-phenylene-vinylene) derivatives and stressed the importance of aggregation phenomena in determining the electronic properties of the polymer films.

Protonation of the pyridine ring induces positive charge into the system. The positive charge may also affect the electronic properties as Wang et al.[2] pointed out in their ion-induced red-shifting of both absorption and emission, although they concluded that the conformational change of the polymer backbone plays a more important role than the positive charge on the metal ion does. Hydrogen bonding is another issue in bipyridine contained system[1] and may be complicated by protonation. It affects inter-ring torsion through intramolecular or intermolecular interactions and consequently the electronic properties. In this paper, we did a theoretical investigation of protonation effects on hydrogen bonding and electronic structures through ring torsion analysis of the protonated bipyridine head-to-head. The evolution of ionization potentials and HOMO/LUMO energy differences as a function of the ring torsion is calculated with AM1 to estimate the effect of π-electron delocalization on these electronic properties of the protonated systems. ZINDO/SCI calculations are carried out to investigate the evolution of the first transition energies as a function of the ring torsion.

This effect is also studied while the bipyridine segment is combined with the vinylene−phenylene−vinylene (VPV) derivatives to investigate the influence upon blending. The protonation effect on the HOMO, LUMO, and the energy gap between them was also investigated in the presence of the counterions. The results show that positive charges on the proton play a very important role in the modification of the electronic structures of the molecules. A comprehensive understanding of the effect of guest ions (protons and metal ions) on the electronic structures of bipyridine-containing polymers was obtained. A general structure of the polymers discussed in this paper is given in Figure 1 named PBPyVPV.

Methodologies

The evolution of the electronic properties as a function of the torsion angle between adjacent rings has already been established.[7] Structures studied in this paper are shown in Figure 1. The steric interaction was mainly discussed on the bipyridine part of all structures. The labeling for all molecules of this part is the same as shown in free base form bipyridine (BPy). A general structure of the polymer mentioned in this paper was given. We first studied the torsion potential of the neutral bipyridine head-to-head (BPy), one-protonated bipyridine (BPy-1H$^+$) and two-protonated bipyridine (BPy-2H$^+$) to investigate the effect of the protonation on the conformation of bipyridine. The ionization potential (I.P.) values, the energy difference between HOMO and LUMO, and the first transition energy were then illustrated as a function of the torsion angle. By applying Koopmans' theorem, the I.P. is simply taken as the inverse of the energy of HOMO. The same calculations were then performed on three bipyridine contained derivatives. The free base form is named BPyVPV shown in Figure 1. The one-

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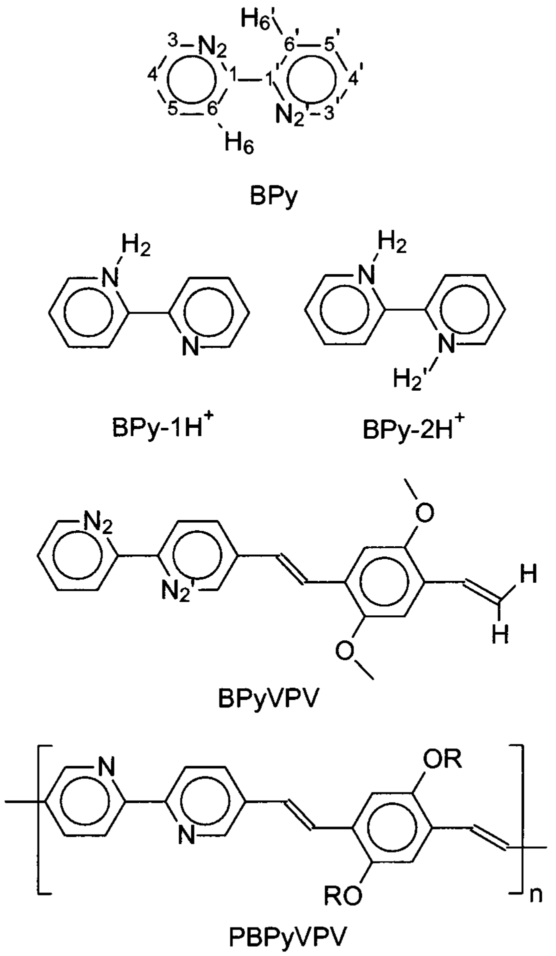

Figure 1. The molecular structures of model molecules and the repeating unit of PBPyVPV.

protonated derivative is named BPyVPV-1H$^+$ and the proton is located on N2′. The two-protonated derivative is named BPyVPV-2H$^+$. The torsion potential, I.P., the energy difference between HOMO and LUMO and the first transition energy were illustrated as the functions of the twisting angle between two pyridine rings. The ending pyridine ring was rotated keeping another pyridine ring and the rest of the segment in the same plane. This imposition was made on the basis of the torsion analysis performed on similar structures.[8] Except this, all geometries were fully optimized with the Hartree−Fock semiempirical AM1 (Austin Model 1) at the RHF level. AM1 was reported to be the most suitable one to study hydrogen bonding.[9] Although there are reports that PM3 gave more accurate geometry for pyridine with respect to *ab initio* calculations,[10,11] the protonation of pyridine gives rise to the existence of the hydrogen bonding, and AM1 has been successfully used in several hydrogen-bonding studies.[12−14] It is also reported that *ab initio* studies of hydrogen-bonding systems are very sensitive to basis set and correction for electron correlation.[15]

The first transition energies (singlet−singlet transition) were calculated on the basis of the AM1 optimized geometries at each torsion angle, using ZINDO/S (the electron interaction terms expressed via the Mataga-Nishimoto potential) with singly excited configuration interaction (CI).[16] The singly excited configurations were generated on the basis of 12 upper occupied and 12 lower unoccupied molecular orbitals for bipyridines and 24 upper occupied and 24 lower unoccupied molecular orbitals for VPV derivatives in order to get stable and reproducible results.

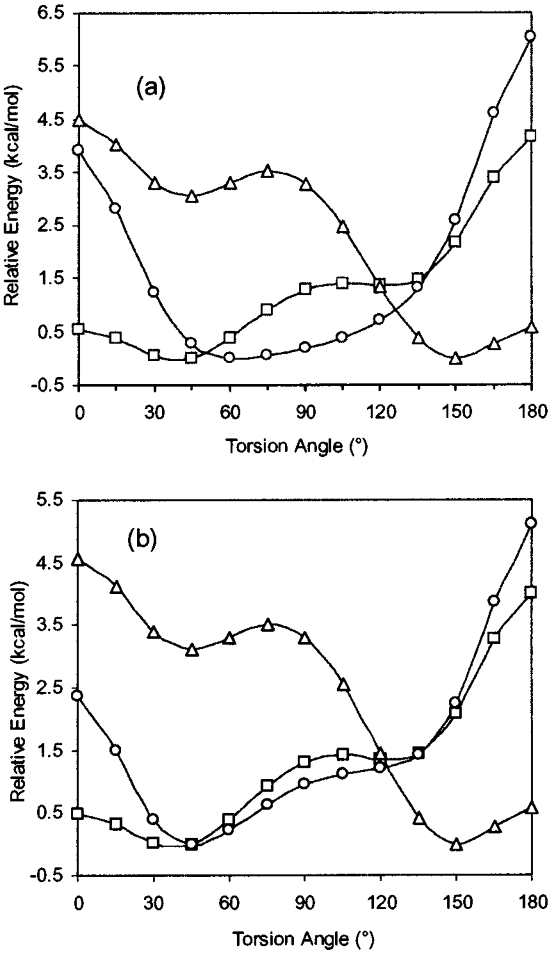

Figure 2. Potential energy curves associated with the torsion of two pyridine rings in (a) BPy (□), BPy-1H$^+$ (Δ), and BPy-2H$^+$ (O); (b) BPyVPV (□), BPyVPV-1H$^+$ (Δ), and BPyVPV-2H$^+$ (O).

When the counterions exist, they are located on the line determined by the protonated nitrogen atom and the proton on it. The distance between the counterion and the proton changes from 2−8 Å. In BPyVPV-1H$^+$, the ending pyridine ring was kept at the twisting angle of 150° with the rest of the part where coplanar conformation was imposed which corresponds to the global minimum of the torsion curve. In case of BPyVPV-2H$^+$, there are two counterions and the distances to the corresponding proton are set equal. The ending pyridine ring was twisted by 60° with the other part which was kept coplanar (the global minimum of the torsion curve). The bond lengths and bond angles were fully optimized for each point on the reaction path.

The counterion is represented by a sparkle. Computationally, a sparkle is an integer negative charge (−1) at the center of the repulsion sphere of form $e^{-\alpha r}$. It is equivalent to borohydride radical, halogen, or nitrate radicals with a zero heat of atomization, no orbitals, and no ionization potential.[17]

The calculations were performed on a Silicon Graphics Octane R10000 workstation at the Computer Center of National University of Singapore using the AMPAC 6.51[17] and Hyperchem 4.5[18] packages.

Results and Discussion

A. Torsion Analysis and Hydrogen Bonding of Bipyridines (Head-to-Head). The potential energy curves of BPy, BPy-1H$^+$ and BPy-2H$^+$ associated with the torsion between two pyridine rings are displayed in Figure 2a. There is some steric interaction between N_2 and H_6′ (same as N_2′ and H_6) at 0°

coplanar conformation as shown in the torsion curve of BPy. The distance r (N_2-H_6'), estimated to be 2.51 Å at this point, increases to 2.75 Å as torsion angles increased to 45°, giving a global minimum around it. As the torsion angle increases further, the potential energy is increased due to the loss of the π-electron delocalization. After 90° torsion, the potential increase is mainly contributed from the steric interaction between H_6 and H_6'. The distances between these two atoms predicted by AM1 are 2.38 Å at 135° and 1.87 Å at 180° conformations, respectively. The interaction between N_2 and H_6' predicted by AM1 is basically steric interaction not hydrogen bonding. This accounts for intermolecular hydrogen bonding playing an important role in the orientation of polybipyridine (PBPy) (head-to-head, model a).[1]

Protonation at N_2 increases the torsion potential at 0° conformation as shown in BPy-1H$^+$ torsion curve, due to the appearance of the steric interaction between H_2 and H_6'. The distance r (H_2-H_6') is predicted to be 1.97 Å at this point. However, the torsion angle of the local minimum is quite comparable with that of the global minimum of BPy, which is also around 45°. This means the steric interaction between H_2 and H_6' exists in a shorter range compared with the steric interaction between N_2 and H_6'. The distance between these two atoms is predicted to be 2.46 Å at 45°, slightly larger than twice the van der Waals radius of hydrogen (2.4 Å). The torsion potential begins to increase as usual after this point but reaches its maximum at 70° not 90° torsion. This is due to the formation of hydrogen bonding between H_2 and N_2'. The global minimum is driven to a more planar conformation with the torsion angle around 150°. The energy barrier toward 180° from this point was largely lowered from 2 kcal/mol in BPy to 0.6 kcal/mol in BPy-1H$^+$. The distances between H_2 and N_2' are 3.44 Å at 75°, 3.22 Å at 90°, 2.56 Å at 135°, and 2.42 Å at 180°. It can be observed that hydrogen bonding formed between the proton and the unprotonated nitrogen plays an important role in the torsion potentials of the one-proton protonated bipyridine.

When both nitrogen atoms in bipyridine molecule are protonated, the energy barriers toward coplanar conformations (at either 0° or 180°) are largely increased due to the steric interactions between hydrogen atoms. The repulsion between hydrogen atoms with more positive charge is reasonably larger (at 180° conformation). This interaction plays an important role in the torsion potential of the two-proton protonated bipyridine.

The torsion potential curves can be used to estimate the contribution of hydrogen bonding toward the 180° coplanar conformation. Based on the above discussion, it can be seen that various interaction (steric and hydrogen bonding) does not exist at the torsion angles ranged from 45° to 75° in potential curves of BPy and BPy-1H$^+$. Let's take the middle point 60° as the reference. Energy differences between this point and 180° conformation are mainly contributed from π-electron delocalization and steric interaction of H_6-H_6' in case of the BPy. In addition to these two effects, hydrogen bonding between H_2 and N_2' contributes to the energy difference in BPy-1H$^+$. It has been concluded that the nitrogen lone pair electrons play no part in the aromatic π ring system[10] and that the protonation only affects deep lying (σ bond) states.[5] Based on this, the contribution of π-electron delocalization to the energy difference between 60° and 180° in BPy and BPy-1H$^+$ should not differ much. Suppose the steric interactions of H_6-H_6' are identical in BPy and BPy-1H$^+$, the contribution of hydrogen bonding to the 180° coplanar conformation can be calculated from the energy difference of BPy and BPy-1H$^+$ between their 60° and 180° conformations. Table 1 lists these relative energies and the estimated hydrogen-bonding contribution to the 180° coplanar conformation.

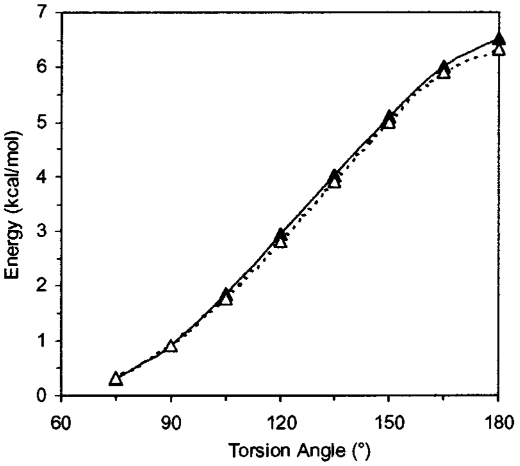

Figure 3. Intramolecular hydrogen-bonding energy as a function of torsion angle between two pyridine rings in BPy-1H$^+$ (▲) and BPyVPV-1H$^+$ (Δ).

TABLE 1: Hydrogen-Bonding (in kcal/mol) Calculation of BPy-1H$^+$ at 180° Conformation

	Relative Energy		
	60°	180°	ΔE
BPy	0.38	4.17	−3.79
BPy-1H$^+$	3.30	0.58	2.72

Hydrogen-Bonding Energy
6.51

The calculated hydrogen bonding in BPy-1H$^+$ at 180° conformation is 6.51 kcal/mol. This value is much closer to 6.7 and 7.3 kcal/mol, which are the experimentally measured and AM1 calculated "cyclization" enthalpies of protonated diaminoethane.[19] Note that 7.3 kcal/mol was obtained from "method B",[19] which compared the enthalpies of the protonated diamine in its bridged conformation with that of the same species in its best extended conformation.

Actually this equation can be used at every point after 60° conformation to calculate the hydrogen-bonding contribution at various ring torsion. The calculated values are displayed in Figure 3 as a function of the torsion angle. The calculated values of its VPV derivatives are also shown for later discussion.

B. HOMO/LUMO Energy of Bipyridines (Head-to-Head). Figure 4a displays I.P. of free and protonated bipyridines. As are expected, they all increase as the torsion angles increase. For free bipyridine and the two-proton protonated ones, the perpendicular conformations yield I.P. values which are 0.5−0.6 eV larger than that of the coplanar conformations. The difference calculated using the same method for biphenyl is 0.76 eV (*ab initio* >1 eV [7]). While for one-proton protonated one, the difference is smaller. It is probably due to the facts that a one-proton substituted molecule breaks the symmetry of the molecule, and the π-electron conjugation at the coplanar conformation has already been reduced. Spatial distribution patterns of the HOMO shows that unprotonated ring has larger contribution than the protonated one in BPy-1H$^+$. On the other hand, the reduction in the delocalization of positive charge destabilizes the HOMO at larger torsion angles. This effect becomes very obvious in BPyVPV-2H$^+$ as its I.P. values decrease as the torsion angle increases (Figure 4b) and will be discussed later. The protonation stabilizes HOMO as the I.P. values largely increase from BPy to BPy-2H$^+$. However, the

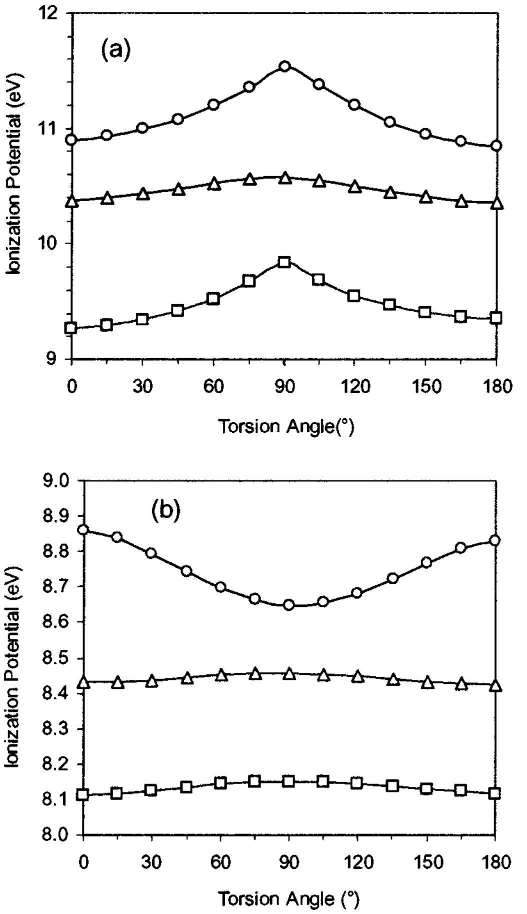

Figure 4. The evolution of I.P. as a function of the torsion angle between two pyridine rings in (a) BPy (□), BPy-1H$^+$ (Δ) (shift down by 3.0 eV), BPy-2H$^+$ (O) (shifted down by 7.0 eV); (b) BPyVPV (□), BPyVPV-1H$^+$ (Δ) (shifted down by 2.1 eV), and BPyVPV-2H$^+$ (O) (shifted down by 4 eV).

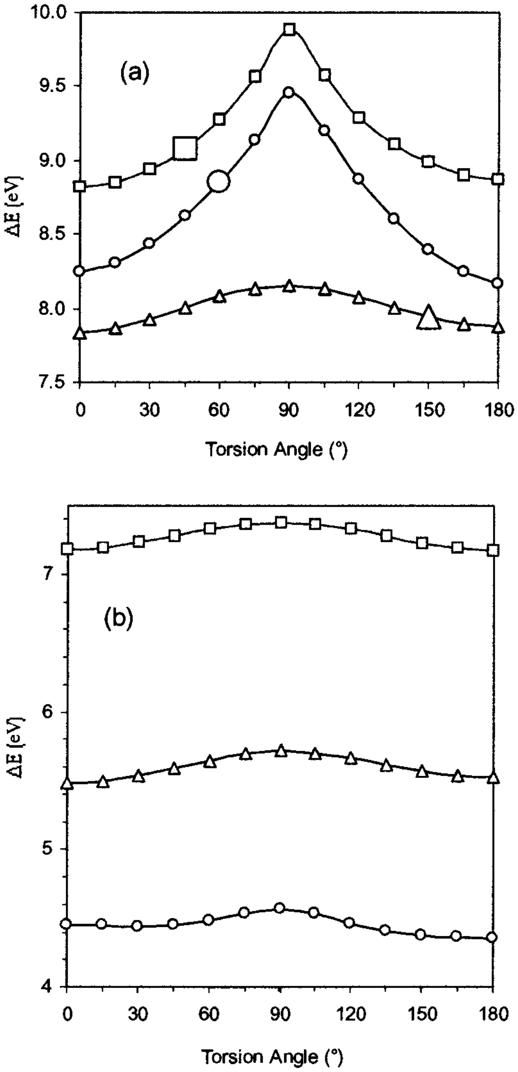

Figure 5. Evolution of the HOMO/LUMO energy difference (ΔE = HOMO−LUMO) as a function of the torsion angle between two pyridine rings in (a) BPy (□), BPy-1H$^+$ (Δ), and BPy-2H$^+$ (O); (b) BPyVPV (□), BPyVPV-1H$^+$ (Δ), and BPyVPV-2H$^+$ (O). Larger markers represent the values corresponding to the global minima.

absolute values of HOMO for the protonated bipyridines are too large without consideration of counterions.

The energy differences ΔE between HOMO and LUMO at the different torsion are displayed in Figure 5a. The ring torsion increases ΔE for both the free base and the protonated bipyridines. Due to the same reasons mentioned above, the effect of the torsion on ΔE of BPy-1H$^+$ is not significant. The values corresponding to the global minimum are labeled with a larger marker. Basically protonation decreases ΔE values and this is consistent with the fact the fully protonated poly(bipyridine) has a red-shift of its absorption maxima comparing with the free base form.[1] The one-proton protonated bipyridine has even smaller HOMO/LUMO energy difference. As mentioned before, an unprotonated ring has a larger contribution to the HOMO. Meanwhile, the protonated ring has a larger contribution to LUMO. This makes the LUMO more stable than HOMO in the case of one-proton protonated bipyridine and consequently decreases their energy difference further.

C. Torsion Analysis of Free and Protonated BPyVPV. The torsion potential curves associated with the inter-ring rotation of bipyridine while it is combined with the vinylene−phenylene−vinylene (VPV) moiety are displayed in Figure 2b. The curves associated with BPyVPV and BPyVPV-1H$^+$ are quite similar to those associated with BPy and BPy-1H$^+$ in Figure 2a. Energy barriers toward 0°, 90°, and 180° conformations are nearly the same in the cases of blending in comparison with those of bipyridines. The same formula is used to evaluate the hydrogen bonding of BPyVPV-1H$^+$ as for BPy-1H$^+$. The calculated curve is displayed in Figure 3 together with that of BPy-1H$^+$ for comparison. The blending slightly lowered the hydrogen bonding. In the case of BPyVPV-2H$^+$, the potential energy curve is quite different from the BPy-2H$^+$. The energy barriers toward 0° and 180° have a large decrease while toward 90° increased compared with corresponding two-protons protonated bipyridine (BPy-2H$^+$). As mentioned before, interaction between positive charges plays an important role in two-proton protonated cases. This interaction should largely depend on the amount of the charges on the hydrogen atoms. The largely reduction in the energy barriers toward coplanar conformations (both 0° and 180°) suggested that the positive charges on the protons are delocalized upon the blending of the bipyridine segment with VPV moiety. The reduction in the positive charge repulsion is also reflected in the increase of the energy barrier toward 90° conformation which is attributed to the loss of the π-electron delocalization.

The ionization potentials of free and protonated BPyVPV are displayed as a function of torsion angle in Figure 4b. For BPyVPV and BPyVPV-1H$^+$, the ionization potential increases slightly as the torsion angle increases. In the case of BPyVPV-2H$^+$, the ionization potential decreases as the torsion angle increases. This is probably due to the loss of the

TABLE 2: ZINDO/SCI Calculated CI Coefficients and Oscillator Strength *f* (a.u.) of various model molecules at 0° and 90° torsions

	0° torsion		90° torsion	
	f	CI coefficient	*f*	CI coefficient
BPy	0.5184	0.624(HOMO→LUMO)	0.2224	0.482(HOMO→LUMO) +0.411(HOMO-1→LUMO+1)
BPy-1H$^+$	0.6042	0.683(HOMO→LUMO)	0.3569	0.585(HOMO→LUMO)
BPy-2H$^+$	0.6909	−0.687(HOMO→LUMO)	0.4810	0.552(HOMO→LUMO) +0.402(HOMO-1→LUMO+1)
BPyVPV	1.7459	−0.645(HOMO→LUMO)	1.3030	−0.641(HOMO→LUMO)
BPyVPV-1H$^+$	0.4998	0.640(HOMO→LUMO)	0.1348	0.654(HOMO→LUMO)
BPyVPV-2H$^+$	1.1343	−0.664(HOMO→LUMO)	0.2559	0.664(HOMO→LUMO+1)

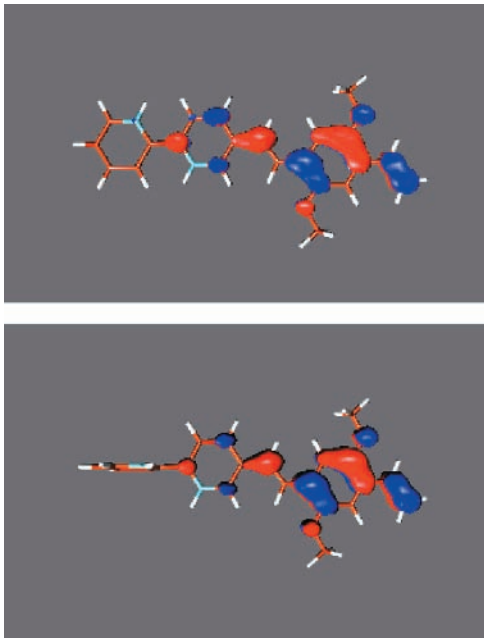

Figure 6. Illustration of HOMOs of BPyVPV-2H$^+$ with the torsion angle between two pyridine rings at 0° (the upper) and 90° (the lower).

delocalization of the positive charges. As shown in Figure 6,[20] the spatial distributions of HOMO of BPyVPV-2H$^+$ are essentially the same at 0° torsion and 90° torsion, which are mainly located on the VPV moieties. However, the net charges on VPV moieties decrease when going from 0° conformation to 90° conformations. The AM1 calculated values are 0.5421 eV and 0.4421 eV, respectively. This indicates that the positive charges on the protons can be delocalized through conjugation. It can stabilize the frontier orbitals like an electron withdrawing substituent.

Figure 5b shows the energy difference between HOMO and LUMO as a function of torsion angle of free and protonated BPyVPV. In all cases, the differences become larger as the torsion angle increase. This indicates that the HOMO/LUMO energy gap (ΔE = HOMO − LUMO) are more related with π-electron delocalization and less with the positive charge delocalization since the positive charge delocalization is quite different in all three cases. The protonation will reduce the energy difference between HOMO and LUMO. As two protons are added, the difference is reduced further. The proton appears to be an electron acceptor substituent. It can stabilize the HOMO and LUMO with the second being the most affected.[21] Consequently, the HOMO/LUMO energy difference is reduced as protons are added. This effect can be more correctly illustrated by calculations in the presence of the counterions.

D. First Transition Properties by ZINDO/SCI. The ZINDO/SCI calculated evolutions of the first transition energies as a function of the torsion angles are illustrated in Figure 7. It could be observed that all sequences and trends in the HOMO/LUMO energy gap discussed above in Figure 5 are reproduced by those of ZINDO/SCI calculated first transition energies. Table 2 lists the ZINDO/SCI transition properties at 0° and 90° conformations. The CI coefficients show that at 0° conformations, the first transition is mainly described by HOMO→LUMO excitations for all model molecules. This contribution slightly decreases when going from 0° to 90° conformations, but is still predominant at 90° conformations in most of the cases. The only exception is in BPyVPV-2H$^+$, which is predominated by the HOMO→LUMO+1 transitions at 90° conformation. However, the transitions at other points on the curve mainly come from HOMO→LUMO excitations. We can conclude that the HOMO→LUMO excitations predominate the first transition in most of the cases we studied. This is true for most of the

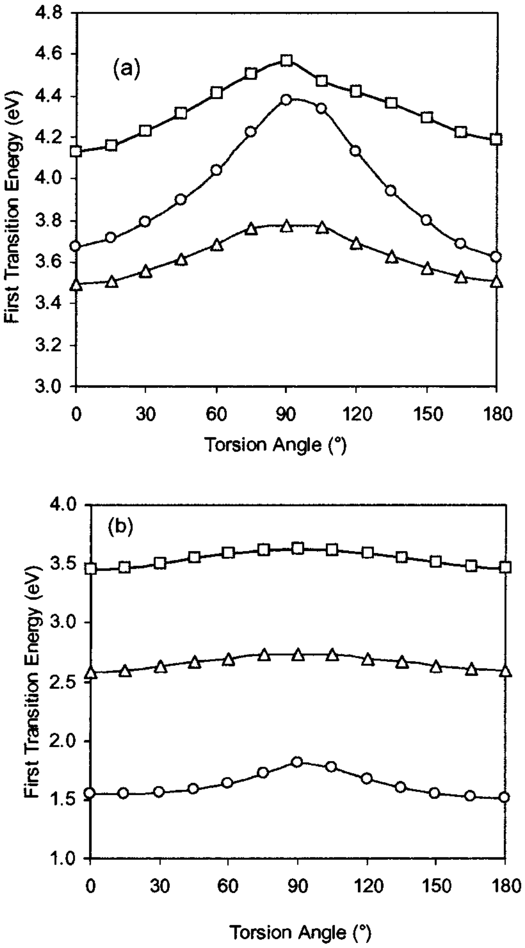

Figure 7. Evolution of the first optical transition energy (by ZINDO/SCI calculations) as a function of the torsion angle between two pyridine rings in (a) BPy (□), BPy-1H$^+$ (Δ), and BPy-2H$^+$ (O); (b) BPyVPV (□), BPyVPV-1H$^+$ (Δ), and BPyVPV-2H$^+$ (O).

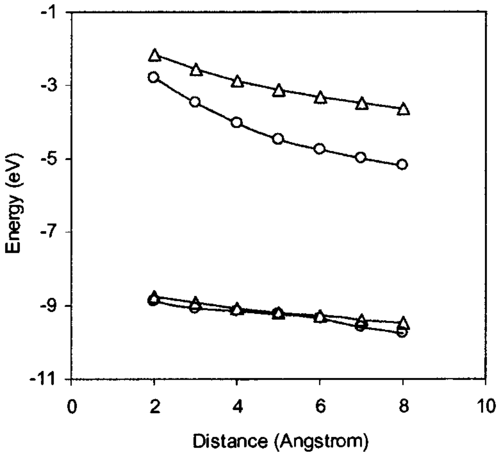

Figure 8. The evolution of the HOMO (lower part) and the LUMO (upper part) as functions of distances between the counterions and BPyVPV-1H$^+$ (Δ) or BPyVPV-2H$^+$ (O).

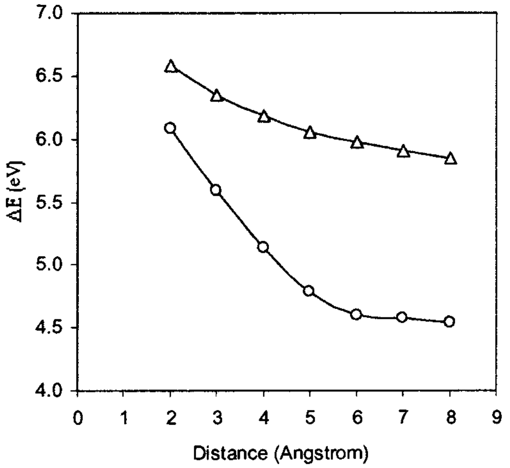

Figure 9. The evolution of Δ*E* (= HOMO − LUMO) as a function of distances between the counterions and BPyVPV-1H$^+$ (Δ) or BPyVPV-2H$^+$ (O).

conjugated systems in their natural states[22] and now we conclude that it is also true for our protonated systems.

E. The Effect of Counterions. All the above results are obtained from the calculations without consideration of the counterions. Taking counterions into consideration, more understanding can be obtained about the protonation effect on UV−Vis behavior of bipyridine contained polymers. Figure 8 shows the evolution of HOMO and LUMO energy levels as a function of the distance between the counterions and the protons. They are all stabilized as the counterions move away from the protons and the limit should be the values obtained from the calculations without counterions as discussed above. On the other hand, when the counterions are very close to the proton, the HOMO and the LUMO energy levels will approach to those corresponding to the free base. Therefore, protonation will stabilize HOMO and LUMO to some extent, depending on the distance of the counterions. It could be seen from the slope of the curves that the LUMOs are more affected than the HOMOs.

As shown in Figure 9, the evolutions of energy gaps between HOMO and LUMO are the same as those of the HOMO and LUMO. Protonation reduces the energy gap to some extent, depending on how far the counterion is. They approach to the value of the free base form as the counterions move toward the protons and as the counterions move away from the protons, the value approach to those obtained without the counterions. This is in agreement with the experimental results of this kind of polymer (Figure 1) will induce red-shift in the UV−Vis absorption upon protonation.[6] This may also be the reason for the metal ion induced red-shifting of the polymers.[2]

Conclusions

In summary, we have carried out torsion analysis on the energy barrier, ionization potential, HOMO/LUMO energy difference (Δ*E* = HOMO − LUMO) and the first optical transition energy of free and protonated bipyridines (head-to-head) as well as their vinylene−phenylene−vinylene derivatives to investigate the protonation effects. No intramolecular hydrogen-bonding interaction exists in the free bipyridine (head-to-head) segment. When one nitrogen atom of the bipyridine segment is protonated, intramolecular hydrogen bonding plays an important role in the ring torsion. The hydrogen-bonding interaction can be evaluated through the comparison of the torsion potentials with those of the free base form. While both nitrogen atoms are protonated, the torsion potentials are predominated by repulsion between positive charges.

The protonation of the nitrogen atom appears to be an electron acceptor on it. Both HOMO and LUMO are stabilized with the second being the most affected. The blending of bipyridine segment with vinylene−phenylene−vinylene derivatives slightly lowers the hydrogen-bonding interaction in BPyVPV-1H$^+$ as well as largely decreases energy barriers toward coplanar conformations in BPyVPV-2H$^+$. This is attributed to the positive charge delocalization to the vinylene−phenylene−vinylene segments. The delocalization of positive charges is also affected by ring torsion as shown in BPyVPV-2H$^+$ that the ring twisting decreases the ionization potential. The energy differences (Δ*E* = HOMO − LUMO) are more affected by π-electron delocalization than positive charge delocalization.

The first optical transitions of all the model molecules are predominated by the HOMO→LUMO excitations especially near the coplanar conformations. As a result, bathochromic shift induced by protonation or metal ion coordinate of corresponding polymers can be explained by the HOMO and LUMO properties.

In the presence of the counterions, the effect of the protonation is more correctly illustrated. As the counterions move toward the protons, the HOMO, LUMO, and the energy difference between them of the protonated BPyVPVs approach to the values of the free base form. As the counterions move away from the protons, these values approach to the limits which correspond to the values we obtained from BPyVPV-1H$^+$ and BPyVPV-2H$^+$ without consideration of the counterions.

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