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Density functional studies of torsion potentials of neutral and protonated bipyridines

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Abstract

The conformational properties of conjugated heteroaromatic bipyridines, pyridyl-pyridiniums and bipyridinium have been investigated using density functional theory (DFT). The molecules studied were neutral 2,2$'$-bipyridine (2,2$'$-bpy), 2,3$'$-bipyridine (2,3$'$-bpy) and 3,3$'$-bipyridine (3,3$'$-bpy) and the singly protonated 3-pyridyl-2$'$-pyridinium (3-py-2$'$-pyH) and 2-pyridyl-2$'$-pyridinium (2-py-2$'$-pyH) and the doubly protonated 2,2$'$-bipyridinium (2,2$'$-bpyH), i.e. typical groups with which longer non-protonated, partially protonated or fully protonated conjugated polypyridine chains with feasible optoelectric properties can be constructed. Comparison of the DFT results including different basis sets has been performed with Hartree–Fock theory and second-order Møller-Plesset perturbation theory (MP2). The DFT (B3LYP/6-31G(d,p)) was found to be adequate to describe the torsion potentials for a force field parametrization. Conformational structures, torsion potential energy surfaces and electrostatic potential (ESP) derived atomic charges have also been calculated. These results are used to parametrize torsion potential parameters in order to improve the description of conformational properties of the molecules using force field based methods. The reparametrized force fields showed the importance of $\cos 4\phi$ term which improved the description significantly for cases which failed without it. Replacing the default atomic partial charges with ESP derived charges improved the description of torsion potentials still. The results allow to gain new insight into importance of accurate force field parameters in the area of conjugated molecules.
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Keywords: Bipyridine; Ab initio; Density functional theory; Torsion potential; Electrostatic potential charges

1. Introduction

In spite of its molecular simplicity, pyridine shows interesting properties due to its heteroaromatic nature combined to its electron deficient nitrogen, see e.g. [1]. It is well known that its nitrogen atom acts as a hydrogen bonding acceptor and it can be coordinated with metal cations and protonated using strong acids [1], although the detailed understanding and modelling of its bondings may be nontrivial and contain subtleties [2]. Due to the specific interactions, pyridine and its derivatives are widely used as constructional units in supramolecular chemistry [3–7]. On the other hand, conjugated oligomers and

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polymers have attracted much interest due to their feasibility in electro- and photo-active materials [8]. Pyridines are important molecules as they can be polymerized as conjugated chain-like molecules [9–11]. Due to their conjugation, polypyridines are luminant in the blue–green spectrum of visible light and are therefore of interest due to their photonic properties [12–14]. It is expected that the colour and optical properties could be further tuned by tailoring the planarity of the rings, i.e. extent of conjugation, as well as the substituents, protonation and coordination of the pyridines [13,14]. In tuning of the optical response and, more generally, in tuning of the molecular materials it is necessary to understand the conformation, configuration and molecular structures of the units to design their packing either in the solid crystalline state, self-organized fluid state or disordered dissolved state [15,12].

Bipyridines are interesting on their own right among the shortest conjugated oligomers, as well as constituent parts of conjugated polymeric polypyridines. The DFT modelling of oligomeric non-protonated pyridines have been performed previously, emphasizing the electronic states, and also predicting the properties of the corresponding polymers [16]. The recent observations that even protonated pyridine moieties may allow feasible photonic properties, their tuning [14] and self-organized structures [15], encourage to develop accurate force fields and to investigate also conformations of the protonated pyridine based molecules. In this work, we study computationally molecular structures of bipyridines (pyridyl-pyridine), the singly protonated pyridyl-pyridiniums and the doubly protonated bipyridinium, see Fig. 1. Other related structures, e.g. 4,4'-bpy, have been omitted as they are not relevant in the context of conjugated polymers. The emphasis is in the torsion angles, which specify the planarity of the molecules and, therefore, the extent of the conjugation, which are crucial for the electro-optic properties for chain-like pyridyl-containing molecules. Results obtained by quantum chemical calculations are used to parametrize the force field parameters. Related studies involving conjugated polymers, e.g. polyacetylene, polydiacetylene, polyparaphenylene, polypyrrole, polypyridine and polythiophene have been carried out in the past [16–18], but in these the main focus
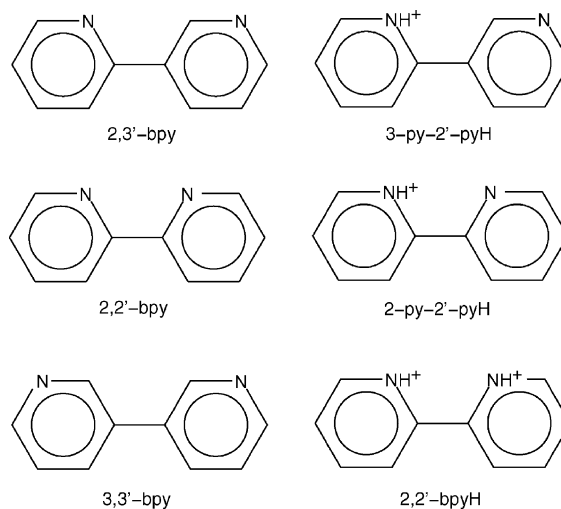

Fig. 1. Chemical structures of investigated bipyridines: $2,3'$-bipyridine ($2,3'$-bpy), $2,2'$-bipyridine ($2,2'$-bpy), $3,3'$-bipyridine ($3,3'$-bpy), 3-pyridyl-$2'$-pyridinium (3-py-$2'$-pyH), 2-pyridyl-$2'$-pyridinium (2-py-$2'$-pyH) and $2,2'$-bipyridinium ($2,2'$-bpyH). The figure also shows the adopted zero value of the torsion angle, corresponding to the *cis* conformation.

has been on the effect of torsion potential on the electronic properties of molecules.

In order to model polymers, molecular mechanics (MM) is often used. In MM the total potential energy is written in terms of bond lengths, bond angles, etc. and this information is collected to an entity called force field. The force field describes the atomistic interactions using potential energy function which contains in general the following terms [19–22]

$$V = \frac{1}{2} \sum_i [F_{ii}(q_i - q_{i0})^2 + F_{ii}^{(3)}(q_i - q_{i0})^3$$
$$+ F_{ii}^{(4)}(q_i - q_{i0})^4 + ...] + \sum_{i<j} F_{ij}(q_i - q_{i0})$$
$$\times (q_j - q_{j0}) + \Sigma V_{tor} + \Sigma V_{q,tor} + \Sigma V_{tor,tor} + \Sigma V_{nb}.$$
$$(1)$$

The first two sums contain the valence part of the force field (q_i denote values of valence bonds and angles while q_{i0} are their reference values). F_{ii} is the harmonic diagonal force constant, $F_{ii}^{(k)}$ the anharmonic diagonal force constant of order k and F_{ij} is the non-diagonal force constant between the coordinates q_i and q_j.

The torsion potential V_{tor} describes rotations about the chemical bonds and is usually represented with cosines as a function of the dihedral angle ϕ

$$V_{\text{tor}} = \sum_n V_n(1 \pm \cos n\phi). \tag{2}$$

In the previous equation, the V_n are the torsion parameters which are to be parametrized in order to reproduce the calculated potential energy surface accurately. Summation is usually truncated after first few terms. For example, in the PCFF force field [23] only terms $n = 1, 2$ and 3 are used. $V_{\text{q,tor}}$ and $V_{\text{tor,tor}}$ in Eq. (1) are cross terms and describe couplings between coordinates q_i and dihedrals ϕ and two dihedrals, respectively.

Interactions between atoms which are not chemically bonded are accounted for by a nonbonded interaction term V_{nb}, usually represented as a combination of a Lennard-Jones type potential for the van der Waals interactions and a Coulomb potential for the electrostatic interactions. For atoms i and j this interaction has the form (also other forms of the function are used)

$$V_{\text{nb}}(r_{ij}) = E_{0,ij}\left[\left(\frac{R_{0,ij}}{r_{ij}}\right)^n - 2\left(\frac{R_{0,ij}}{r_{ij}}\right)^6\right]$$
$$+ k\frac{e_i e_j}{\varepsilon(r_{ij})r_{ij}} \qquad n = 9 \text{ or } 12 \tag{3}$$

where r_{ij} is the distance between the atoms, $E_{0,ij}$ and $R_{0,ij}$ are parameters dependent of the atom type, e_i and e_j are the partial charges of the atoms, $\varepsilon(r_{ij})$ is the dielectric constant, which in some force fields is distance dependent, and k is a constant.

2. Computational details

All quantum chemical computations were performed with GAUSSIAN 98 [24] software on an SGI Origin 2000 computer. Individual torsion potentials were obtained for each molecule by performing a constrained geometry optimization of the structure as a function of inter-ring C–C dihedral angle which was varied between 0 and 180° in 15° steps. Zero angle refers to the planar structure where both nitrogens are on the same side, i.e. the *cis* conformation, see Fig. 1. Geometries were fully optimized without any

constraints for the minimum energy structures as well as for the transition state structures.

Geometry optimizations were performed using density functional theory (DFT) [25,26] with B3LYP functional [27] and 6-31G(d,p) basis set. For comparison, the torsion potential of 2,3′-bpy was computed using four additional basis sets: 3-21G, 6-31G, 6-31+G(d,p) and 6-311G(d,p). Additionally, the torsion potential was also investigated using HF and MP2 methods with 6-31G(d,p) basis set.

Atomic partial charges were calculated from the electrostatic potential (ESP) with CHelpG scheme [28] at the global minimum energy structures using B3LYP/6-31G(d,p) method. However, it should be kept in mind that, especially for conjugated π-systems, atomic partial charges may be conformation dependent [29].

The MMs part was performed using the INSIGHT II and DISCOVER [30] software on an SGI Origin 2000 computer. The PCFF force field was used in these calculations. In the original PCFF force field no distinction was made between the inter-ring C–C bond and the intra-ring C–C bonds in the molecules. Therefore, a new atom type for the carbon atoms forming the C–C bond between the rings was defined. The parameters for the central C–C torsion and stretching potentials were optimized independently from the potentials of the aromatic rings. The optimizations of torsion parameters were performed by calculating the conformational energy putting the torsion parameters of the inter-ring C–C bond equal to zero and varying the dihedral angle in steps of 15°. Using these structures, the potential energy was then optimized on the quantum chemically calculated torsion potential using the least-squares method to determine the optimal fit. In this way deficiencies in the rest of the potential are partly corrected by the torsion potential.

3. Results and discussion

In Figs. 2–5 the torsion potentials as a function of the torsion angle are presented as relative torsion potentials where the optimized global minimum energy structure is taken as a zero level. Due to the symmetry of the molecules, it is sufficient to study
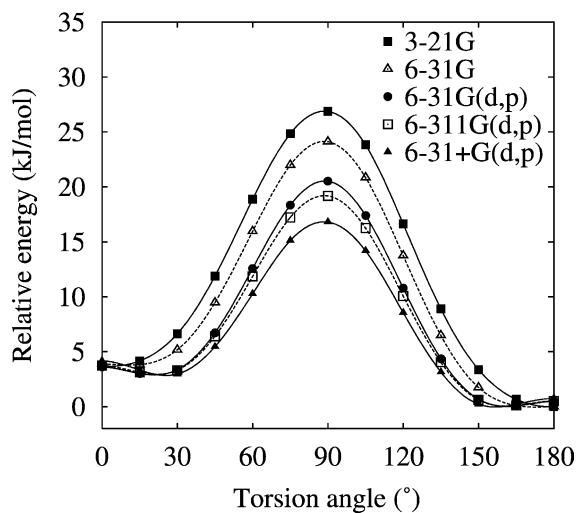
Fig. 2. Comparison of relative torsion energies with different basis sets for 2,3′-bpy with B3LYP functional.

Fig. 4. Comparison of relative torsion energies for 2,2′-, 2,3′- and 3,3′-bpy computed with the B3LYP/6-31G(d,p) method.

torsion angles from 0 to 180°. The conformation in which the torsion angle is less than 90° is taken as the *cis* conformation, and the conformation where the torsion angle is greater than 90°, is the *trans* conformation.

To begin with, the influence of basis sets and computational methods were investigated with 2,3′-bpy. The effect of the basis set on the conformational behaviour was investigated by comparing the torsion
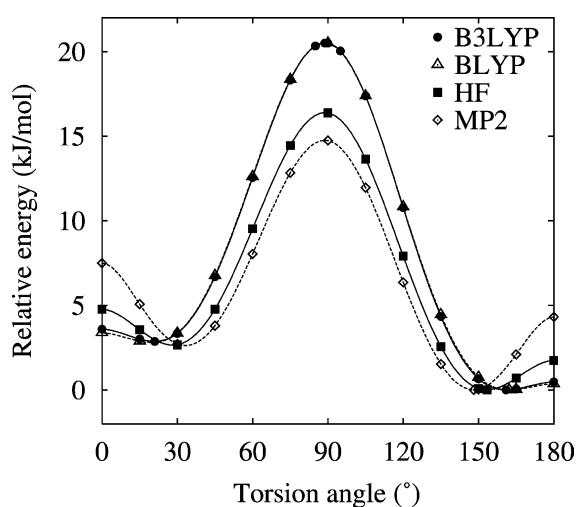
energies calculated with the common 3-21G, 6-31G, 6-31G(d,p), 6-31+G(d,p) and 6-311G(d,p) basis sets. In these calculations, B3LYP functional was used. Results are shown in Fig. 2. Compared to the larger basis sets, the 3-21G and 6-31G were found to be inadequate to describe the torsion potential in all conformations. The torsion angle corresponding to the transition state is located correctly, but the barrier energy is overestimated compared to the 6-31G(d,p)

Fig. 3. Comparison of relative torsion energies with different methods for 2,3′-bpy with the 6-31G(d,p) basis set.
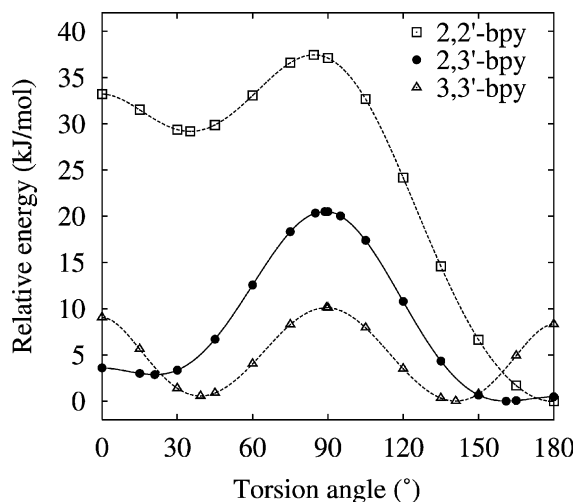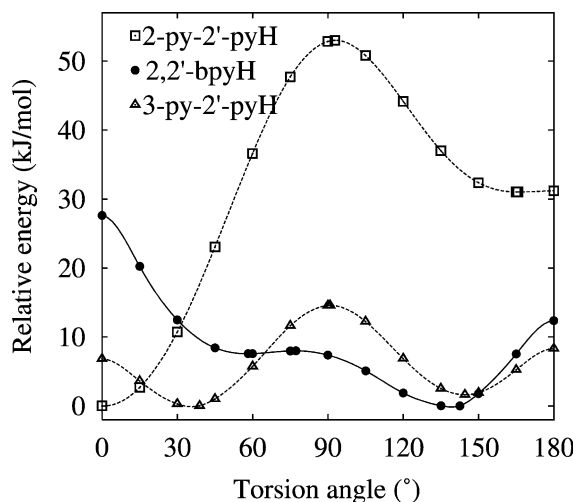

Fig. 5. Comparison of relative torsion energies for singly protonated 2-py-2′-pyH and 3-py-2′-pyH and doubly protonated 2,2′-bpyH computed with the B3LYP/6-31G(d,p) method.

basis set results. For the 3-21G and 6-31G basis sets, the suggested torsion potential is less accurate and leads even to qualitatively incorrect description close to planar conformations. For example, the optimized structures both in the *cis* and *trans* conformations would correspond to a completely planar molecular geometry. This is most probably due to the inability of these basis sets to account for the steric effects arising from the hydrogens. Incorporation of the polarization functions to all atoms is thus necessary to produce correct behaviour of the torsion potential. Addition of one more Gaussian valence function with the 6-311G(d,p) basis set lowers the energy at the transition structure by about 1 kJ/mol, but it has practically no effect on the torsion potential closer to planar conformations. Similarly, addition of diffuse functions to non-hydrogen atoms with the 6-31+G(d,p) basis set lowers the energy at the transition structure by about 4 kJ/mol, which is not insignificant, but on the other hand the computational cost increases quite radically with diffuse functions in the basis set. In conclusion, the 6-31G(d,p) basis set was found to be adequate for the purposes of this study.

Next, computational methods were compared by repeating the torsion potential calculation with DFT using BLYP functional [31,32], and with the HF and MP2 methods. Here the 6-31G(d,p) basis set was used. The results are shown in Fig. 3. All methods produce qualitatively similar form of the torsion potential. BLYP and B3LYP methods predict practically the same relative energies and the inclusion of Hartree–Fock exchange term has no significant effect. While HF and MP2 results are rather close to each other for the orthogonal conformation, and DFT results are higher in energy compared to HF and MP2 methods, this situation is reversed in planar conformations where MP2 energy is notably highest, while HF and DFT results are closer together. With HF and MP2 methods the torsion angles and the energies corresponding to the minima are produced in good agreement with each other. The DFT methods predict the minima to have somewhat more planar conformations. Similarly, the DFT methods give few kJ/mol lower barriers for the planar conformations than the ab initio methods. This is in agreement with earlier studies of conjugated systems, which indicate that DFT methods somewhat overestimate the delocalisation energy [33], and therefore, produce more planar

structures and lower orthogonal barriers than ab initio methods. As a compromise between accuracy and computational cost, the B3LYP/6-31G(d,p) level of theory was chosen for rest of the calculations.

Using the B3LYP/6-31G(d,p) method, the conformational behaviour of selected bipyridines, pyridyl-pyridiniums and bipyridinium are presented in Table 1 and Figs. 4 and 5.

2,2'-bipyridine has a global planar *trans* minimum and a distorted local *cis* minimum at 35.1° which is 29.2 kJ/mol above the global minimum. The barrier at the orthogonal conformation is 37.5 kJ/mol with respective to the global minimum. When

Table 1
Selected structural parameters and relative energies of optimized minimum energy structures of neutral and protonated bipyridines computed with the B3LYP/6-31G(d,p) method

		Torsion angle (°)	C–C bond length (Å)	Relative energy (kJ/mol)
2,2'-bpy	TS	0.0	1.499	33.2
	cis	35.1	1.494	29.2
	TS	84.4	1.503	37.5
	trans	180.0	1.490	0.0
2,3'-bpy	TS	0.0	1.488	3.6
	cis	21.0	1.485	2.9
	TS	88.8	1.496	20.5
	Trans	161.0	1.486	0.0
	TS	180.0	1.488	0.5
3,3'-bpy	TS	0.0	1.488	9.1
	cis	39.3	1.480	0.6
	TS	89.5	1.491	10.1
	trans	140.9	1.480	0.0
	TS	180.0	1.488	8.3
2-py-2'-pyH	cis	0.0	1.480	0.0
	TS	92.8	1.497	53.0
	trans	165.7	1.479	31.0
	TS	180.0	1.480	31.2
2,2'-bpyH	TS	0.0	1.488	27.6
	cis	58.2	1.489	7.6
	TS	77.3	1.496	8.0
	trans	136.2	1.484	0.0
	TS	180.0	1.486	12.4
3-py-2'-pyH	TS	0.0	1.469	6.8
	cis	35.1	1.468	0.0
	TS	88.8	1.496	14.6
	trans	144.6	1.465	1.6
	TS	180.0	1.469	8.3

2,2′-bipyridine is singly protonated the positions of the minima change (Fig. 5). The planar *cis* minimum becomes the global minimum, most probably due to the attractive electrostatic interaction and/or intramolecular hydrogen bonding between the protonated and non-protonated nitrogens. The orthogonal barrier is increased to 53.0 kJ/mol and the relative energy of the *trans* minimum is 31.0 kJ/mol. When protonated once more, i.e. doubly protonated, the energy differences decrease and the global *trans* minimum is located at 136.2°. The second *cis* minimum at 58.2° is very shallow and the highest barrier 27.6 kJ/mol is now in planar *cis* conformation.

2,3′-bipyridine has two shallow minima at 21.0 and at 161.0°, the former *cis* mimimum being 2.9 kJ/mol higher in energy compared to the latter global *trans* minimum. The orthogonal barrier is 20.5 kJ/mol and the planar barriers are almost nonexistent. When the nitrogen atom in 2-position is protonated, the *cis* minimum at 35.1° becomes the global minimum, but the *trans* minimum at 144.6° is only 1.6 kJ/mol higher in energy. Due to the protonation, the orthogonal barrier is reduced to 14.6 kJ/mol but, on the other hand, both planar minima are significantly increased.

3,3′-bipyridine torsion potential resembles more 2,3′-bipyridine than 2,2′-bipyridine. It has two minima at 39.3 and at 140.9°, the former *cis* mimimum being 0.6 kJ/mol higher in energy compared to the latter global *trans* minimum. The orthogonal barrier is 10.1 kJ/mol but now the planar barriers are almost of similar magnitude, 9.1 and 8.3 kJ/mol.

The results agree with the assumption that the protonation has crucial effect on the conformational properties of bipyridines. This demonstrates that the Coulomb term is one of the most important potential energy terms in molecules with polar groups. In order to examine the validity of the electrostatic parameters used in force field methods, it is important to compare them to atomic charges derived from the ESPs, which are obtained with quantum chemical calculations. In force field methods the atomic partial charges are often obtained using the bond increment method (see e.g. Ref. [20]), where predetermined fractional atomic partial charges are added for each bond type. While this method works reasonably well for many non-conjugated systems, its validity is not

obvious in all cases, especially for conjugated molecules containing electronegative heteroatoms, like in the molecules treated in this paper.

The ESP atomic charges calculated with the CHelpG scheme at the global minimum energy conformations of each molecule are shown in Fig. 6 for the non-protonated bipyridines and in Fig. 7 for the protonated bipyridines. In the non-protonated bipyridines, the *ortho* and *para* carbon atoms (relative to nitrogen) have positive and *meta* carbon atoms negative partial charges, respectively. In protonation the positive charge is partly distributed to the aromatic ring and the absolute values of the charges become smaller. It is clear that the bond increment method cannot give atomic partial charges in an agreement with ESP atomic charges. Two other commonly used methods, the charge
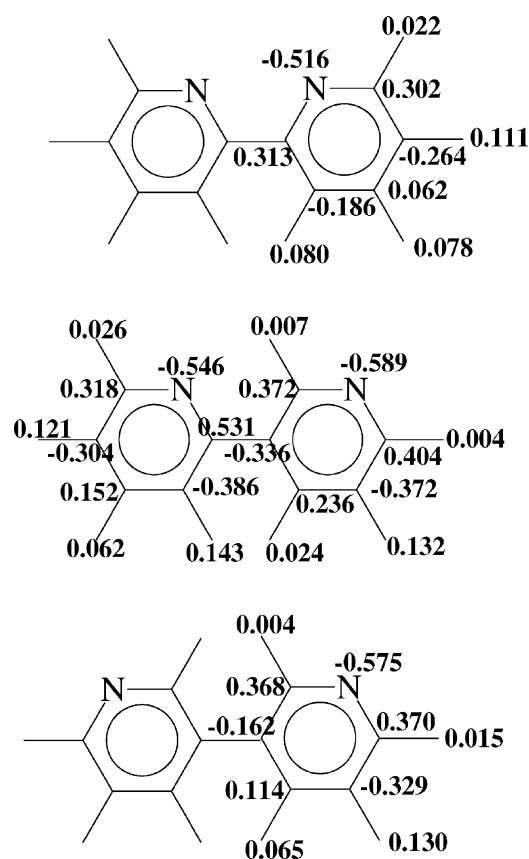

Fig. 6. The ESP based atomic charges calculated with the CHelpG scheme for non-protonated bipyridines (atoms having equivalent charges due to the symmetry are not labelled).
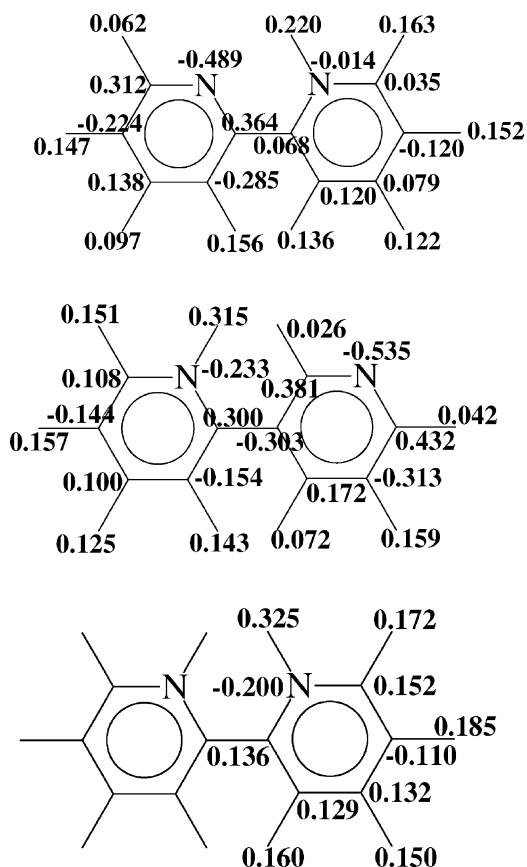
Fig. 7. The ESP based atomic charges calculated with the CHelpG scheme for protonated bipyridines.
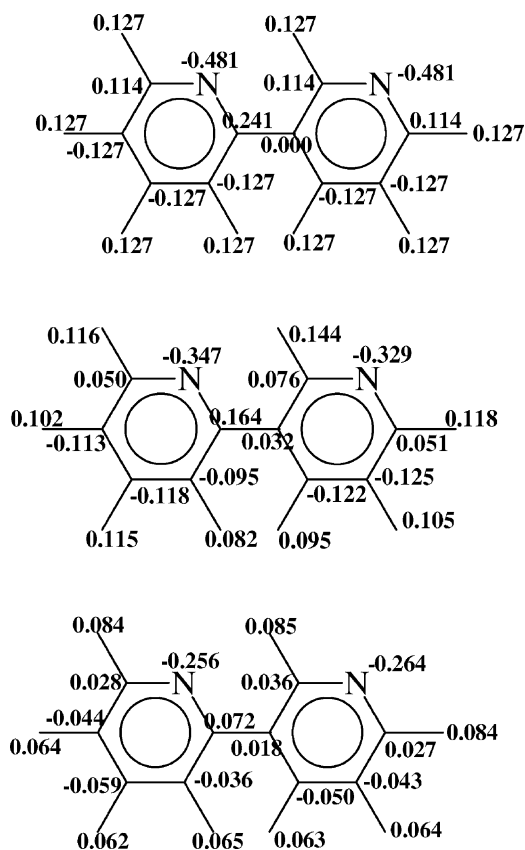

Fig. 8. The atomic partial charges calculated with the bond increment (top), charge equilibration (middle) and charge equalization (bottom) methods for 2,3′-bpy.
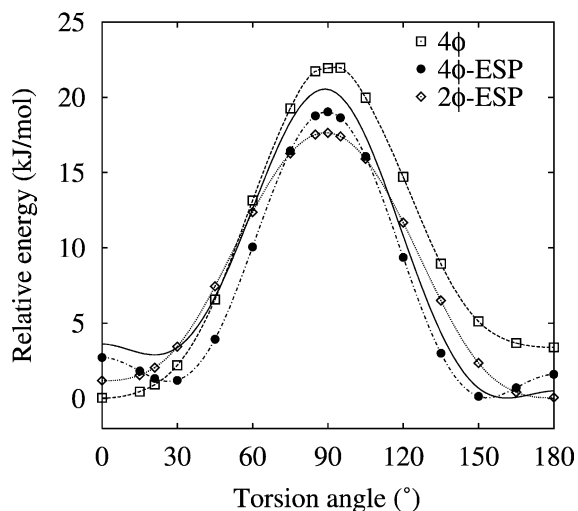
equilibration method by Rappe and Goddard [34] and charge equalization method by Gasteiger and Marsili [35] were tested. Both methods take the electronegativity and the neighbouring atoms into account, and are thus theoretically more sound than the bond increment method. Also these methods, however, failed to give atomic partial charges in a reasonable agreement with ESP atomic charges. The results for 2,3′-bipyridine are shown in Fig. 8. Comparing with the ESP charges in Fig. 6, it can be seen that none of the other methods can reproduce the position dependent variation of the carbon charges. Also the absolute values of the charges were much too low, especially for the charge equalization and charge equilibration methods. Therefore, when a realistic molecular electrostatic field is needed for heteroaromatic molecules with nitrogen atom in the aromatic

Fig. 9. Fitted torsion potentials for 2,3′-bpy. The quantum chemical torsion potential is shown as a solid line without markings.

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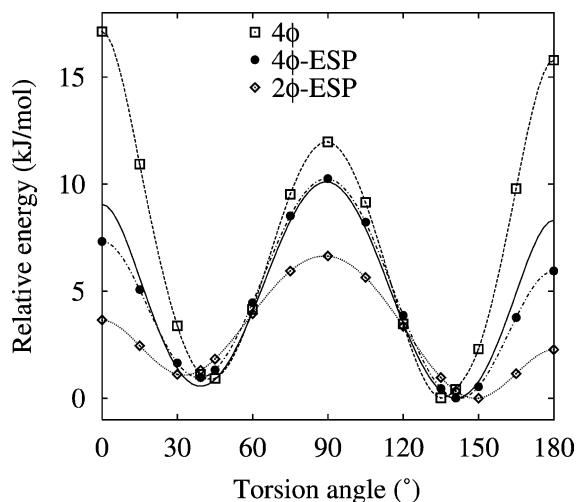

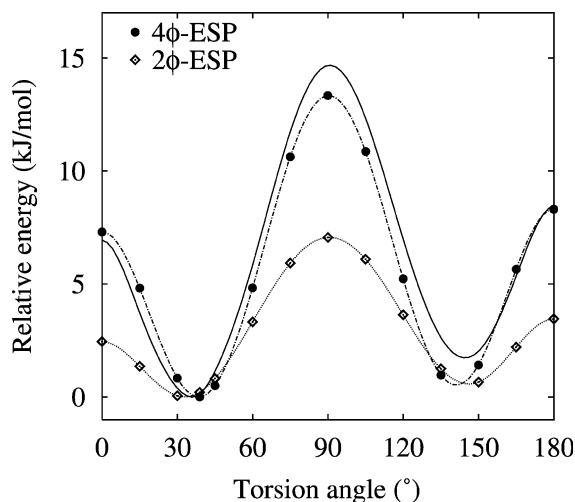Fig. 10. Fitted torsion potentials for 3,3'-bpy.

Fig. 12. Fitted torsion potentials for protonated 3-py-2'-pyH.

ring, a more accurate treatment of charges is required.

Bond stretching term of the inter-ring C–C bond was adjusted to give bond lengths in a reasonable agreement with quantum chemical results. The reference value of the coordinate was chosen to 1.482 Å, and the stretching force constant to 250 kcal/Å^2.

When the torsion potential parameters were optimized using the original PCFF charges determined by the bond increment method and only including V_1 and V_2 torsion parameters, it became evident that a reasonable torsion potential model for

bipyridines could not be obtained. This is in an agreement with our earlier studies of related molecules [36]. Therefore, V_4 parameters were added into the torsion potential model. The results were somewhat improved, but were still unsatisfactory, as can be seen form Figs. 9 and 10 (4ϕ). For 2,3'-bipyridine the relative energies of the minima are calculated in wrong order and for 3,3'-bipyridine the planar barriers are significantly overestimated. Protonated bipyridines were excluded from this optimization. It should, however, be noted that in the PCFF force field only V_1, V_2 and V_3 parameters are allowed, and that there is
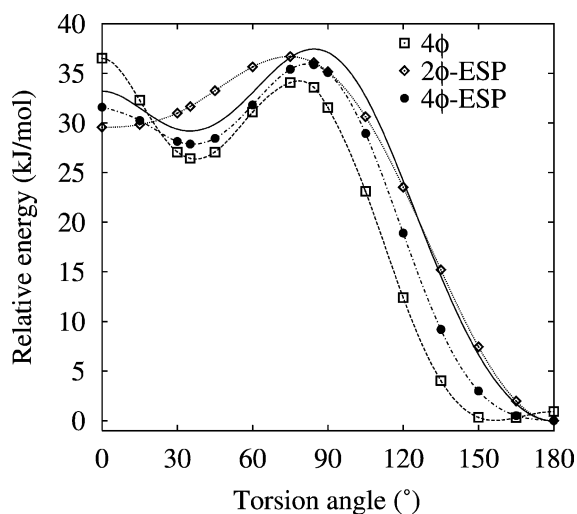

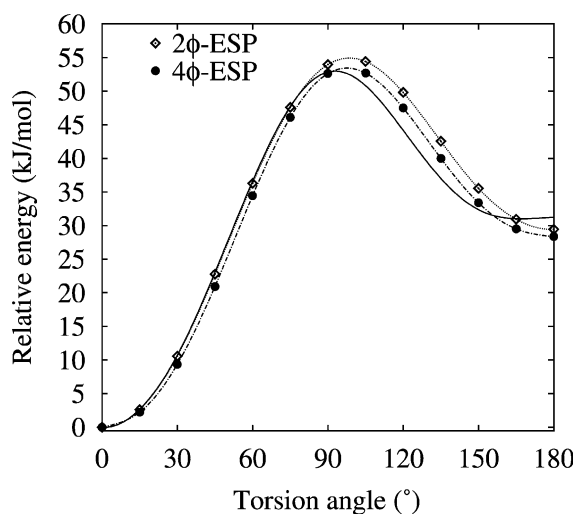Fig. 11. Fitted torsion potentials for 2,2'-bpy.

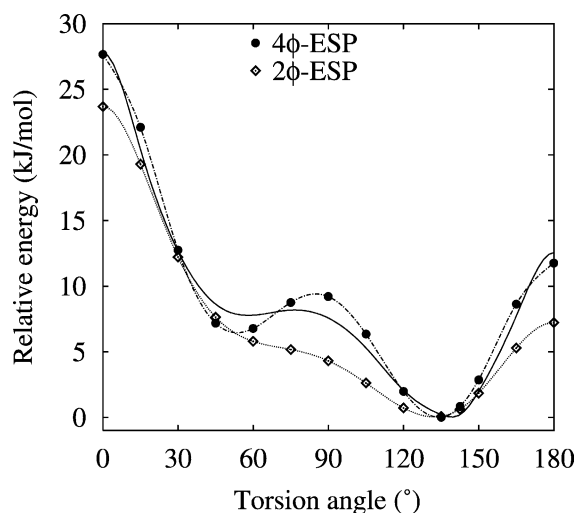Fig. 13. Fitted torsion potentials for protonated 2-py-2'-pyH.

Fig. 14. Fitted torsion potentials for doubly protonated 2,2′-bpyH.

no physical reason to use threefold V_3 terms in torsion potentials for a sp^2-sp^2 bond.

A satisfactory overall fit, including protonated bipyridines, was obtained when the bond increment charges were replaced by ESP atomic charges, as shown in Figs. 9–14 (4ϕ-ESP). Since the potentials are to be added into the PCFF force field, we optimized also the torsion parameters with ESP atomic charges but including only V_1 and V_2 terms (2ϕ-ESP). Now the most significant deviations from

the B3LYP/6-31G(d,p) results were for 3,3′-bipyridine and for the protonated 3-pyridyl-2′-pyridinium. For these molecules both the planar and orthogonal barriers become notably too low, as can be seen from Figs. 10 and 12. The optimized torsion potential parameters are given in Table 2 both with and without V_4 term and with both bond increment (original PCFF) and ESP atomic charges. It should be noted that these parameters are intended to be used in the PCFF force field.

4. Conclusions

In this paper we have investigated conformational behaviour of bipyridines and protonated bipyridines at B3LYP/6-31G(d,p) level of theory and compared computational methods and basis sets. Protonation and the extent of it turned out to have a profound influence on the conformational properties of the molecules. For example, in the case of 2,2′-bipyridine the minimum energy structure of the non-protonated molecule has a completely planar *trans* conformation, when the molecule is singly protonated it has also a planar structure but in the *cis* conformation, whereas in the doubly protonated state the planar conformation is not energetically preferred. Such a behaviour may have an important role in the optical properties of

Table 2

Torsion potential parameters (kcal/mol) for original PCFF force field and corresponding optimized parameters obtained using the ESP atomic charges[a]

Potential	With original PCFF charges			With ESP charges		
	V_1	V_2	V_4	V_1	V_2	V_4
cp cw cw cp	− 0.2731	0.5274		− 0.4356	0.6540	
cp cw cw np	0.1893	1.2257		0.4164	0.8379	
np cw cw np	0.4988	− 0.1041		0.4412	1.2153	
cp cw cw nh				− 0.6500	1.3193	
np cw cw nh				1.5954	3.0941	
nh cw cw nh				− 0.7864	0.7682	
cp cw cw cp	− 0.8748	0.5034	− 0.2981	− 0.2956	0.6522	− 0.1242
cp cw cw np	0.1796	1.2571	0.1466	0.5220	0.6522	− 0.1732
np cw cw np	0.7813	− 0.3694	− 1.0969	0.5026	1.2332	0.0068
cp cw cw nh				− 0.5437	1.4073	− 0.2273
np cw cw nh				1.5397	2.9169	0.3731
nh cw cw nh				− 0.6460	0.6708	0.0000

[a] In INSIGHT II and DISCOVER programs the potential parameters are given in units of kcal/mol.

polypyridines. The torsion potentials were also used to optimize torsion parameters for the inter-ring bond to be used in the PCFF force field. Neither bond increment, charge equilibration, nor charge equalization methods were capable of giving atomic partial charges in a reasonable agreement with ESP atomic charges. When the bond increment charges were replaced with ESP atomic charges, a transferable set of torsion parameters could be found for the inter-ring bond. It was also shown that in addition to one- and two-fold torsion terms, fourfold terms are crucial to achieve an accurate description of torsion behaviour of the conjugated molecules studied here.

Acknowledgements

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