

# Accurate Force Field Development for Modeling Conjugated Polymers

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The modeling of the conformational properties of conjugated polymers entails a unique challenge for classical force fields. Conjugation imposes strong constraints upon bond rotation; planar configurations are favored, but the concomitantly shortened bond lengths result in moieties being brought into closer proximity than usual. The ensuing steric repulsions are particularly severe in the presence of side-chains, straining angles and stretching bonds to a degree infrequently found in non-conjugated systems. We herein demonstrate the resulting inaccuracies by comparing the LMP2-calculated inter-ring torsion potentials for a series of substituted stilbenes and bithiophenes to those calculated using standard classical force fields. We then implement adjustments to the OPLS-2005 force field in order to improve its ability to model such systems. Finally, we show the impact of these changes on the dihedral angle distributions, persistence lengths, and conjugation length distributions observed during molecular dynamics simulations of poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) and poly 3-hexylthiophene (P3HT), two of the most widely-used conjugated polymers.

## I. INTRODUCTION

Conjugated polymers are of great interest for their potential use in photovoltaic devices and light emitting diodes. Although these polymers can be quickly and cheaply produced from abundant materials, significant advances in efficiency are required for them to compete economically with currently deployed solar cell and display technologies.<sup>1</sup> Future developments of novel applications for conjugate polymer materials will depend on a detailed understanding of the coupling between conformational and electronic properties.

Following synthesis, conjugated polymers are typically cast into thin films. The polymer's chemical structure as well as casting conditions influence polymer morphology within the film, and features of this morphology then influence the material's optoelectronic behavior.<sup>2</sup> Although the important role of polymer morphology in modulating this behavior is well-recognized, the precise morphology and its dependence on structural variations remains elusive. Molecular modeling provides a way to examine these effects at a level of detail that is generally unavailable experimentally. However, results from modeling will only be as good as the representation of the physical forces at work in these polymers.

Molecular force fields have historically been developed and refined for use with biomolecules, which generally do not contain extensive conjugation. In conjugated systems, the combined effect of shorter inter-atomic bond lengths and a bias towards planar configurations leads to unusually strong steric clashes, especially for conjugated bonds that link together ring moieties, such as those found in polyphenylene vinylene (PPV) and polythiophene (PT). These systems test the limits of current force fields; even small errors in the modeling of forces

involved in bond-stretching, angle-bending, torsion rotations, and steric interaction can result in inappropriate modeling, especially of the energies involved in rotations about the inter-ring torsions. However, accurate modeling is particularly important for those dihedral angles since the inter-ring torsion degree of freedom is one of the most influential in terms of both the polymer's large-scale fluctuations and folding as well as the length over which its electrons delocalize. Thus, appropriate modeling of the arrangement and nature of the material's chromophores depends upon an accurate representation of the forces influencing these inter-ring bond rotations.

We begin this paper by discussing the effects of inadequate potentials in Section II. Then, in Section III, we calculate LMP2-derived potential energy surfaces for the inter-ring torsions of a series of substituted stilbene and bithiophene derivatives, which constitute the basic dimers of the ubiquitous polyphenylene-vinylene (PPV) and polythiophene (PT) polymers. After demonstrating the inability of the standard OPLS-2005 potential to adequately reproduce these LMP2 curves in Sections IV & V, we then test and discuss a variety of adjustments to the OPLS-2005 potential in Section VI & VII. Finally, in Section VIII we consider the influence of our adjustments on sampled torsion angle distributions, persistence lengths, and conjugation length distributions during molecular dynamics simulations of poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) and poly 3-hexylthiophene (P3HT).

## II. EFFECTS OF INACCURATE POTENTIALS

Modeling conjugated polymers with classical force fields that were designed primarily for non-conjugated systems may result in unphysical results along several

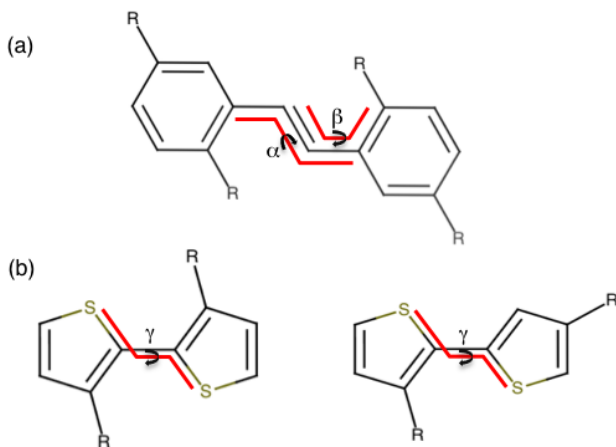


FIG. 1. (a) Stilbene with two substituted R-groups. The torsions of interest,  $\alpha$  and  $\beta$ , are marked by the arrows, and the atoms defining them are highlighted by the red bars. In this study, we consider R = H, Me (methyl), Et (ethyl), OH (hydroxyl), OMe (methoxy), OEt (ethoxy), and OiPr (isopropoxy). (b) 3,3' (left) and 3,4' (right) disubstituted bithiophenes. The torsion of interest,  $\gamma$  is again marked by an arrow and the defining atoms are indicated by the red bars. For bithiophene, we consider R=H, Me, Et, and iPr (isopropyl). Note that no R-group atoms are highlighted by the red indicator bars.

dimensions. In general, energy minima may be located inaccurately, the shapes of energy basins may be too narrow or too wide, and energy barriers may be over- or under-estimated. In particular, errors may be expected in the following:

- Close steric interactions,
- Bending and stretching under strain,
- Rotations around conjugated bonds,
- Planarity of conjugated segments,
- $\pi$ - $\pi$  stacking interactions.

As a result, errors may arise in the modeling of optimal conformations, molecular fluctuations, folding behaviors, aggregation events, and the electronic properties of conjugated polymers and their aggregates. In addition, we consider here only fixed charge force fields, thus errors resulting from the failure to explicitly treat polarization effects may also be expected.

By far the largest errors that existing force fields manifest when applied to conjugated polymers reside in the potential energy curves around torsional bonds connecting aromatic moieties. The most straightforward approach to reducing these errors is to fit torsional coefficients to an accurate quantum chemical potential surface. Such an approach can work reasonably well if the goal is to model one specific polymer. However, in modeling conjugated polymers, we seek to assist in the design

and optimization of new polymeric materials with specific functional properties. This task may require the modeling of thousands of chemical variants of the aromatic cores, linker regions, and side chains, but performing accurate quantum chemical calculations for each of these variants and then refitting the torsional parameters appropriately would entail an enormous and arguably prohibitive amount of work. Hence, the goal of conjugated force field development must be to develop a model and set of parameters that are transferable and can be used to model the entire set of envisioned polymers. Lack of transferability is a defect that goes beyond the manifestation of large errors for a single polymeric chemistry (which could be repaired by refitting torsions); it is indicative of problems within the broader scope of the force field as applied to the types of chemistry under study. In the present case, the key challenge is to properly represent conjugation effects while at the same time balancing those effects against the steric interactions that arise from side chain clashes. As we shall see below, even the best performing current force fields experience difficulties in this regard. In this work, we suggest some approaches to solving the problem, and demonstrate that, at least for the set of examples considered here, these approaches are transferable and display considerable success in reducing the errors to acceptable levels. Beyond transferability, a second (and more subtle) problem is scalability; will an approach that works for a small number of anecdotal examples enable the development of a larger and more comprehensive set of parameters that exhibit a similar level of error control and transferability across a broader range of chemical functionality? We argue that the improvements proposed below are readily scalable to broad chemical coverage, and hence provide a path forward towards robust and accurate modeling of conjugated polymer systems.

### III. LMP2-CALCULATED POTENTIALS

To begin our analysis, the torsional potentials of bithiophene and stilbene were calculated at the LMP2/cc-pVTZ(-f)//B3LYP/6-31+G\*\* level. This was achieved by sampling the torsion of interest (see Fig. 1) at 10 degree intervals from 0 to 180 degrees while optimizing all remaining degrees of freedom. For stilbenes, both  $\alpha$  and  $\beta$  angles were examined, although  $\alpha$  was examined only for the unsubstituted stilbene. Since the majority of PPV backbone linkages are in the *trans* configuration, and the barrier to rotation is quite high,  $\alpha$  remained in this configuration ( $\alpha = 180^\circ$ ) during the minimizations as  $\beta$  was sampled at various dihedral angles. For bithiophenes, the sole inter-ring torsion,  $\gamma$ , was considered for unsubstituted as well as 3,3'- and 3,4'-disubstituted species. 3,4'-disubstituted bithiophenes are representative of the polymer linkages in regioregular polythiophenes, while regiorandom polythiophenes also contain 3,3'- and 4,4'-disubstituted bithiophene moieties. 4,4'-

disubstituted bithiophenes are not considered as they lack the more severe steric clashes present in 3,3'- and 3,4'-disubstituted bithiophenes and are presumably more amenable to treatment with the unmodified OPLS force field.

All geometries were initially optimized at the B3LYP/6-31+G\*\* level since B3LYP is known to give good geometries at a reasonable computational cost compared to other methods. Subsequently, single-point energy calculations were performed at the LMP2/cc-pVTZ(-f) level. This level of theory was chosen as it gave good agreement with the *ab initio* results reported by Raos *et al.* for bithiophene<sup>3</sup> and Kwasniewski *et al.* for stilbene.<sup>4</sup> We assumed that this good agreement for stilbene and bithiophene would be transferable to functionalized stilbenes and thiophenes as well. Furthermore, while the majority of the energetic profiles explored do not contain substantial energetic contributions due to dispersion interaction, the profile for rotation around  $\alpha$  does. Specifically, in the *cis* configuration, there is substantial  $\pi - \pi$  stacking, making it necessary to use a method like LMP2 which is capable of accurately treating such interactions. Energies were computed every ten degrees between 0° and 180° (see Methods for details). These results are shown in Figures 2, 3 & 4, where the thick blue lines represent the LMP2 results.

Stilbene and bithiophene may be considered as 2-mer model systems of PPV and PT systems, respectively. It is important to address the transferability of results derived with these 2-mer model systems to the study of full-length PPVs and PTs. Crystal structures of both PPVs and PTs show these polymers in roughly planar conformations.<sup>5,6</sup> Our calculations on stilbene certainly agree with the experimental results, where minima are located at 0° and 180° (*cis*-planar and *trans*-planar, respectively). (See LMP2 curve in Fig. 3b.) However, for bithiophene, we witness minima at approximately 40° and 150° (*cis*-distorted and *trans*-distorted, respectively, see Fig. 4a), not 0° and 180° as might be suggested by the observation of planar geometries in crystal structures.

Darling and Sternberg<sup>7</sup> have published an extensive study testing the transferability of *n*-mer model systems, where  $n = 2, 4, \dots, 14$  to full-length PTs. In agreement with our results, they find that 2-mers preferentially adopt distorted, instead of planar, minima. Notably, this is in disagreement with the torsions seen in crystals of longer PTs. They also find that increasing the size of the model *n*-mer system to  $n \geq 4$  produces a qualitative change in the potential energy profile, and the minima are now at the planar, not distorted, conformations, in agreement with what is found in the crystal structures of PTs. Naïvely, this suggests that 2-mers produce results in qualitative disagreement with the crystal structure, as the 2-mers prefer distorted conformations while the polymers in crystals adopt planar conformations. If true, one would conclude that the strict use of 2-mers is insufficient to model systems of longer PTs. However, it is important to note that Darling and Sternberg used a different level

of theory (B3LYP/6-311G(d,p)//B3LYP/3-21G\*) than that employed here. They note that, when optimizations are performed in bases larger than 3-21G\*, all *n*-mers adopt distorted minima, in contrast to the planar minima obtained with 3-21G\*.

Finally, in performing their scans on *n*-mers with  $n \geq 4$ , Darling and Sternberg fixed all  $\gamma$  dihedral angles (except the one under investigation) in their planar conformations, suggesting that they have located local, rather than global, minima. To test this, we have also performed scans on the 4-mer at the LMP2/cc-pVTZ(-f)//B3LYP/6-31+G\*\* level of theory, since, as mentioned above, this combination gives good agreement with previously reported *ab initio* results.<sup>3</sup> Here, we varied all three  $\gamma$  torsions and we were able to reproduce Darling and Sternberg's results. Indeed, we find that if all torsions are held fixed in their planar conformations while varying only the central torsion, overall planar conformations for the 4-mer are preferred over distorted conformations. Importantly however, we also found that varying all torsions, not just the central torsion, gives a global minima wherein all torsions prefer to adopt the *cis*-distorted over *cis*-planar conformation. Further, the *trans*-planar conformation is only 0.5 kcal/mol higher than the *trans*-distorted conformation, a value well within the error for such a level of theory.

Our results are in qualitative agreement with those of Darling and Sternberg and both sets of results suggest that these polymers adopt distorted, not planar, geometries natively. Stated another way, as both 2-mers and 4-mers adopt non-planar minima (within the error of the method employed to study these torsions), we posit that non-planar minima are not unique to 2-mers, but are likely be a feature of *n*-mers in general. This further suggests that crystal packing induces the planarity observed in crystal structures. Importantly, the 2-mers appear to be accurately capturing the non-planar nature of the minima in these longer 4-mer systems. Thus in contrast to Darling and Sternberg, we argue that 2-mers represent an appropriate model system for the study of PTs, as they reproduce the qualitative behavior of larger *n*-mers at the LMP2/cc-pVTZ(-f)//B3LYP/6-31+G\* level while requiring only a fraction of the computational cost. For this reason, all parameterizations reported herein were performed using dimers.

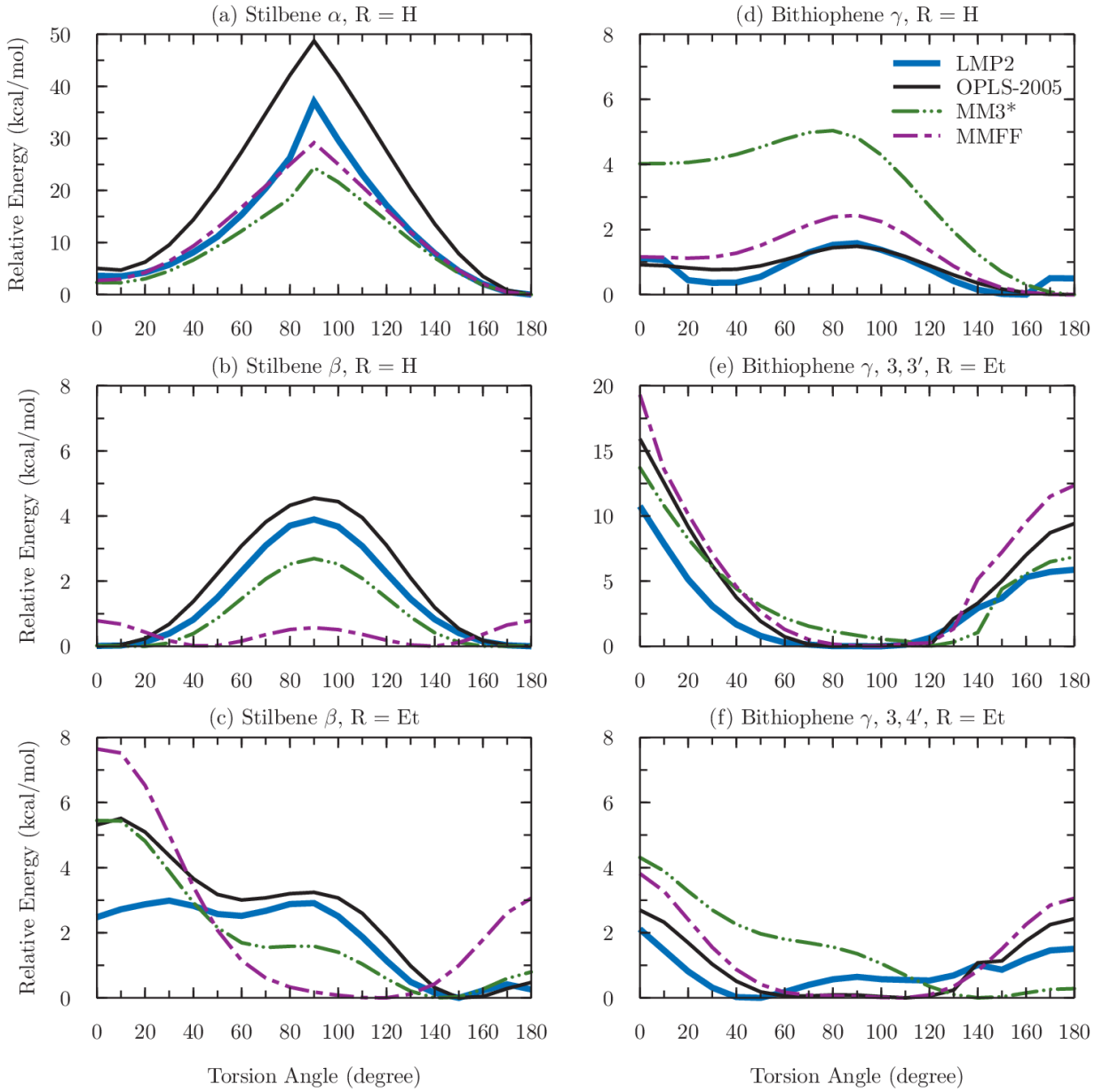


FIG. 2. Comparison of torsion potentials calculated by LMP2, OPLS-2005, MM3\*, and MMFF for (a) the  $\alpha$  torsion (see Fig. 1) of unsubstituted stilbene, (b) the  $\beta$  torsion of unsubstituted stilbene, (c) the  $\beta$  torsion of ethyl-substituted stilbene, (d) the  $\gamma$  torsion of unsubstituted bithiophene, (e) the  $\gamma$  torsion of ,3,3'-diethyl-bithiophene, and (f) the  $\gamma$  torsion of 3,4'-diethyl-bithiophene.

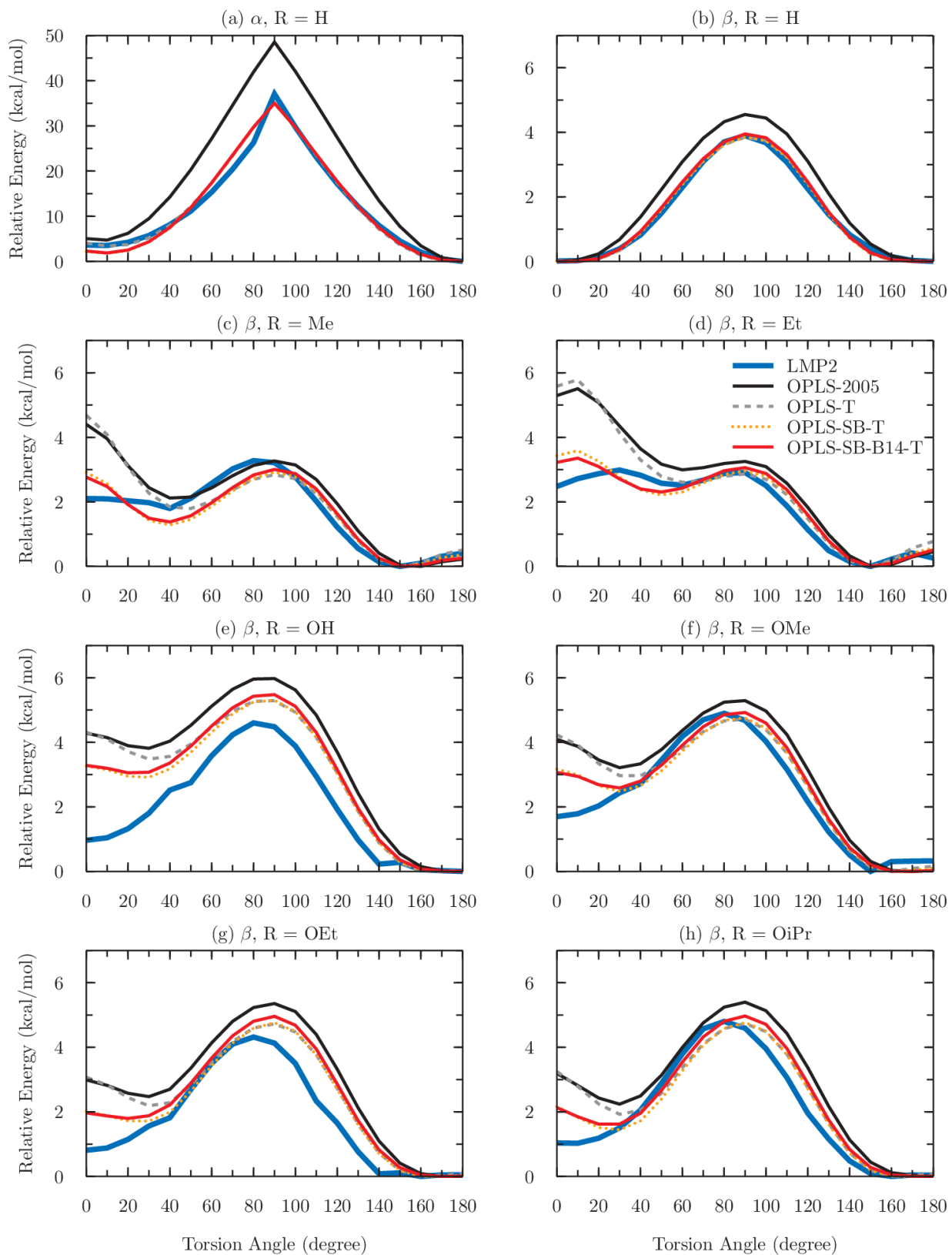


FIG. 3. Comparison of LMP2 and various OPLS-2005 potentials for disubstituted-stilbenes. (a) shows the potential around the  $\alpha$  torsion angle (see Fig. 1) for unsubstituted stilbene, while (b-h) show the potential around the  $\beta$  torsion angle for various R-substituted stilbene species: (b) R=H, (c) R=Me, (d) R=Et, (e) R=OH, (f) R=OMe, (g) R=OEt, and (h) R=OiPr.

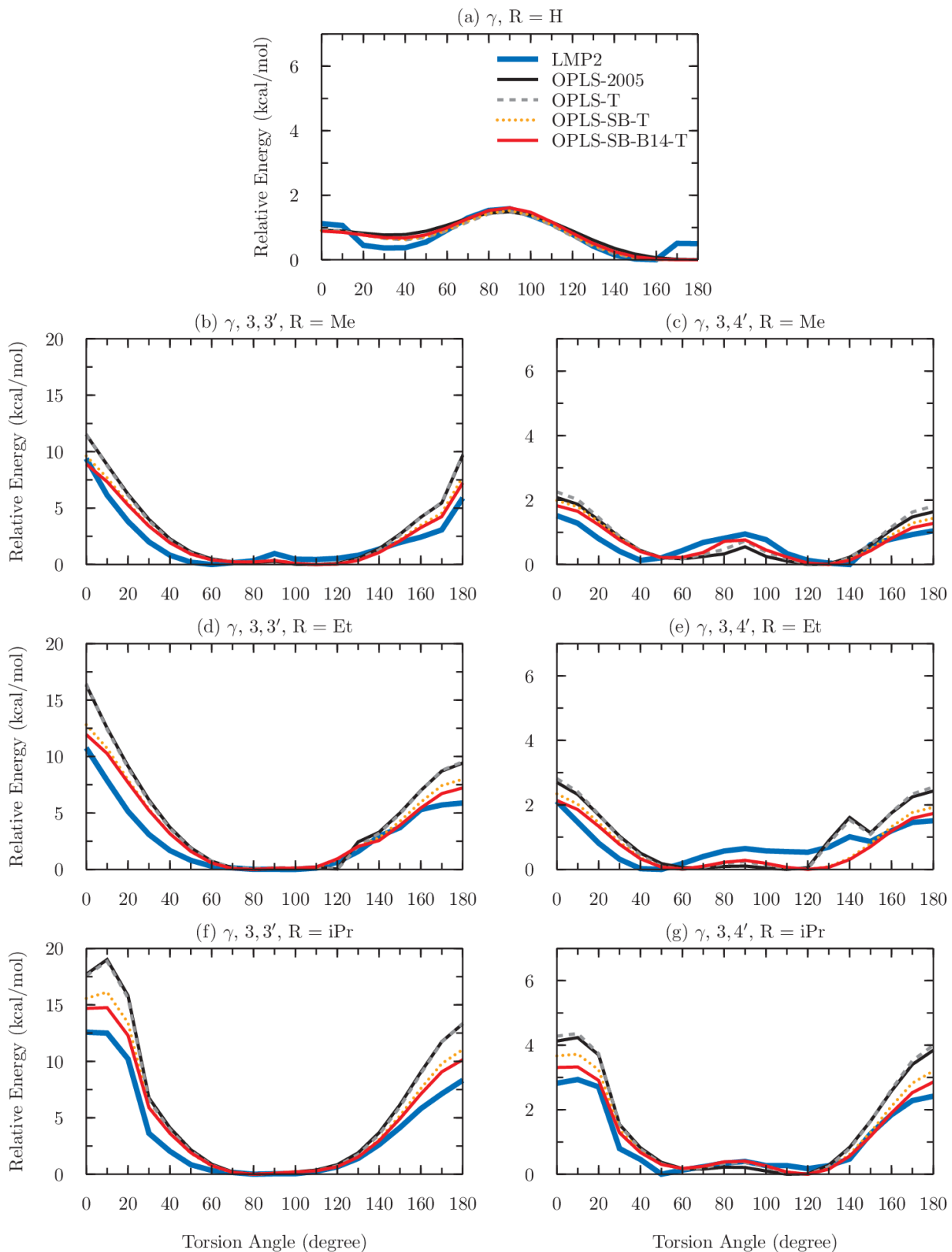


FIG. 4. Comparison of LMP2 and various OPLS-2005 potentials for disubstituted-bithiophenes. (a) shows the potential around the  $\gamma$  torsion angle (see Fig. 1) for unsubstituted stilbene, while (b-d) show the potential around the  $\gamma$  torsion angle for various disubstituted bithiophene species: (b) 3,3'-dimethyl-bithiophene, (c) 3,4'-dimethyl-bithiophene, (d) 3,3'-diethyl-bithiophene, (e) 3,4'-diethyl-bithiophene, (f) 3,3'-diisopropyl-bithiophene, and (g) 3,4'-diisopropyl-bithiophene.

#### IV. OPLS-2005-CALCULATED POTENTIALS

Previous studies on conjugated polymers have generally made use of either the OPLS (Optimized Potentials for Liquid Simulations<sup>8</sup>) or the MM3 potentials.<sup>6,8-11</sup> MM3 provides additional terms and iterative bond order calculations that are not available in OPLS, but the additional computational costs do not appear to be justified. In fact, work by Marcon and coworkers has demonstrated that potentials based on OPLS-2005 outperformed those based on MM3 and more recent refinement and modeling efforts have shifted to OPLS-based potentials.<sup>6,12,13</sup>

Our initial investigations confirmed that the OPLS-2005 all atom force field provides a good starting representation of the inter-ring torsion potentials for stilbene and bithiophene. Figure 2 shows the superiority of OPLS-2005 over MM3<sup>9,14</sup> and MMFF<sup>15</sup> in reproducing the potentials derived from LMP2 for a subset of the torsions we consider here. MM3\*, while performing reasonably well in Figures 2a, 2b, & 2e, greatly overestimates the energies for torsions of less than 90° in Figures 2c, 2d, & 2f. MMFF performs reasonably well in Figures 2a, 2d, 2e, & 2f (although not as well as OPLS-2005 in these last three cases), however the locations of its minima in Figures 2b & 2c are qualitatively incorrect. Overall, OPLS-2005 best reproduces the LMP2 results, especially considering that its over-estimate of the barrier in Figure 2a can be easily corrected with softened torsion parameters.

Even though OPLS-2005 performs reasonably well, there are significant limitations to its accuracy (see Figures 2, 3, & 4). As a result, various optimizations have been made to OPLS for the study of oligothiophenes. However, until recently, the goal was to design a force field specific to each oligomer under investigation.<sup>10,12</sup> The most recent of these optimizations instead aims to improving OPLS’s ability to model a wide range of oligothiophenes by focused on crystalline oligothiophenes<sup>6</sup>. In this work, Moreno and coworkers reassigned electrostatic charges and refit various dihedral potentials to better reproduce known crystal configurations. However, the inter-ring torsion potential was optimized for a quarterthiophene without any side-chains,<sup>6</sup> as was also the case in work done to optimize the AMBER force field for polythiophenes.<sup>16</sup>

As a result, these studies do not address the problems we discuss herein, namely the inaccuracies that emerge upon side-chain substitution. In addition, in Ref. 6, the torsional term is simply adjusted so that it negates all remaining error between the results of their modified OPLS calculation and those of their target B3LYP calculation<sup>6</sup>, an approach that requires an altered functional form of the torsion potential and is likely to result in a force field that is overly optimized to the specific training conditions. In particular, this sort of parameterization is unlikely to be transferable as side-chains are added, a principle objective of the present effort.

Just as for the LMP2 calculations, minimized energies

were computed every ten degrees between 0° and 180° using OPLS-2005 (see Methods for details). These results are represented by the solid black lines in Figures 3 & 4.

#### V. COMPARISON OF LMP2 AND OPLS-2005 POTENTIALS

*Stilbene Derivatives.* There is a striking difference between the resulting plots from unsubstituted stilbene (Figures 3a & 3b) and its substituted derivatives (Figures 3c - 3h). For unsubstituted stilbene, the difference between the two curves for the  $\alpha$  angle is substantial, with OPLS-2005 overestimating the LMP2-derived barrier height at 90° by 11.9 kcal/mol. For the  $\beta$  angle, the overestimation is modest, just 0.7 kcal/mol at the barrier. However, both these discrepancies are symmetric around 90°, making them amenable to simple adjustments in the standard OPLS-2005 torsion parameters (see below). In contrast, the difference between the two potentials for the substituted stilbenes are less symmetric, and consistently show the greatest discrepancy around 0 – 10°. It is precisely at these angles that the competition between steric clashes (intensified by the short length of the conjugated single bond) and the conjugation-induced planarity is most severe. In the *trans* configuration of  $\alpha$ ,  $\beta$  angles close to 180° avoid this problem, as the substituted group is in close contact with a hydrogen atom instead of the carbon atom it encounters at 0°. Interestingly, increasing the bulkiness of the substituent group, for example from methyl, to ethyl, finally to isopropyl, does not necessarily increase this discrepancy. A quantitative comparison of the different potential energy curves can be seen in Table I, where half of the structures have root-mean-square deviation (RMSD) values larger than 1.0 kcal/mol.

*Bithiophene Derivatives.* The comparison between LMP2- and OPLS-2005-calculated potential energy curves for unsubstituted bithiophene can be seen in Fig. 4a. Within chemical accuracy (typically taken as errors  $\leq 1$  kcal/mol), the two approaches result in essentially the same curve. When considering the disubstituted molecules, however, substantial differences emerge, particularly for the 3,3'-disubstituted species. (See Figures 4b - 4g.) For these molecules, near-planar configurations where the  $\gamma$  angle is close to *either* 0° *or* 180° result in substantial error; unlike the stilbene derivatives, where the substituted group only makes close contact with a hydrogen in the 180° configuration, the substituted groups in bithiophene-derivatives make close contact with a bulkier sulfur atom. Naturally, the problem is exacerbated in the 3,3'-disubstituted species, as in these cases, the substituted moieties come into even closer contact with each other at configurations close to 0°. In general, increasing the bulkiness of the substituent group does increase the discrepancy for these bithiophene-derivatives (see Table I). Again, the OPLS-2005-calculated energies of several of these structures have a RMSD of greater than 1.0 kcal/mol from the

Structures	OPLS-2005	OPLS-T	OPLS-SB-T	OPLS-SB-B14-T
<b>Stilbenes</b>				
$\alpha$ , R=H	8.47	1.29	1.51	1.49
$\beta$ , R=H	0.54	0.10	0.08	0.11
$\beta$ , R=Me	0.79	0.84	0.43	0.38
$\beta$ , R=Et	1.16	1.18	0.39	0.34
$\beta$ , R=OH	1.75	1.43	1.08	1.18
$\beta$ , R=OMe	0.97	0.87	0.54	0.54
$\beta$ , R=OEt	1.22	0.95	0.67	0.76
$\beta$ , R=OiPr	0.97	0.78	0.49	0.52
<b>Bithiophenes</b>				
$\gamma$ , R=H	0.26	0.21	0.22	0.23
$\gamma$ , R=Me, 3, 3'	1.61	1.60	0.95	0.82
$\gamma$ , R=Et, 3, 3'	2.42	2.39	1.38	1.13
$\gamma$ , R=iPr, 3, 3'	3.06	2.98	1.79	1.31
$\gamma$ , R=Me, 3, 4'	0.40	0.44	0.30	0.24
$\gamma$ , R=Et, 3, 4'	0.58	0.59	0.42	0.38
$\gamma$ , R=iPr, 3, 4'	0.71	0.76	0.41	0.25

TABLE I. RMSD between LMP2- and OPLS-calculated potential energy curves, in kcal/mol.

LMP2-computed energies.

*Consequences for Polymer Modeling.* These results give a comprehensive picture of the substantial errors in the torsional potential that arise when utilizing the OPLS-2005 force field to model conjugated polymers. These large discrepancies indicate that for both stilbene and bithiophene derivatives, such as the commonly used polymers MEH-PPV and P3HT, sampling with the standard OPLS-2005 potential would significantly bias the results away from the appropriate equilibrium distributions suggested by our LMP2 calculations. The location of the global minimum within the torsional potential is generally well-approximated by OPLS-2005. However, the barriers are typically overestimated and, in the stilbene derivatives, the local minimum that is present near  $0^\circ$  in the LMP2-derived potential is often modeled as a maximum in the OPLS-2005-derived version. In addition, the quality of the OPLS-2005 potential varies significantly with changes to the side-chains, rendering it less useful for comparing behaviors between structural variants of these polymers.

## VI. OPLS POTENTIAL ADJUSTMENTS.

### A. Torsion Adjustments.

Upon first examination, it may appear that we can simply make adjustments to the torsional potential in order to fix these discrepancies. However, a closer look at Figure 1 suggests otherwise. The thick red bars highlight the four atoms that define each dihedral angle, making it clear that, for the torsions under consideration, no atoms from the substituted moieties are part of these four-atom sets. As a result, any torsional adjustments we could make to improve the potentials for substituted stilbene and bithiophene would then, by necessity, den-

igrate their performance for the unsubstituted species. Due to the substantial differences we observe between the unsubstituted and substituted molecules (see above), it seems unlikely that such an approach would be able to resolve the problems that occur when computing minimized energies for the near-planar configurations of these substituted species.

Nevertheless, it is clear that some kind of adjustment to the torsional potential is required, particularly for the  $\alpha$  angle of stilbene, and thus the dashed grey lines in Figures 3 & 4 and the second column in Table I display the results of the approach described above. We adjusted the OPLS-2005 torsion parameters to better approximate the torsion potentials for the unsubstituted molecules and applied the same adjustments to their substituted derivatives (see Methods for details).

For the unsubstituted stilbene torsions, the barrier height is reduced to match the LMP2 result when using what we term the “OPLS-T” force field (OPLS with torsional adjustment). The torsion potentials for  $\alpha$  and  $\beta$  resulting from this OPLS-T force field are nearly identical to the LMP2-derived curves. For the unsubstituted bithiophene torsion,  $\gamma$ , a slight adjustment was made to narrow the peak, but the match to the LMP2 curve is very good with either the OPLS-2005 or the OPLS-T force field.

However, for the substituted derivatives of both stilbene and bithiophene, it is clear that these adjustments alone are not sufficient. Although the OPLS-T-calculated barrier heights for stilbene derivatives are an improvement over the OPLS-2005-calculated heights, the substantial discrepancies near  $0^\circ$  remain and even become larger in a few cases, trends that can also be seen in the RMSD values in Table I. For the substituted bithiophene derivatives, in keeping with the very minor adjustment that were made to the  $\gamma$  torsion potential, almost no differences are seen between the OPLS-2005 and OPLS-T curves, and thus their discrepancies with



the LMP2-derived curve persist. It is clear that, in addition to changes in the torsional parameters, other adjustments to OPLS-2005 will be needed in order to properly model these molecules.

It should be noted here, however, that the required torsional potential adjustment depends on other adjustments made to the potential. Thus, in the subsequent sections, as we test additional changes to the OPLS-2005 potential, we refit the torsion to the unsubstituted case after each additional adjustment. So by “OPLS-X-T” we denote the OPLS-2005 potential with an adjustment made to X followed by an adjustment of the torsional potential that results in its fitting to the LMP2-calculated potential for the unsubstituted stilbene and bithiophene torsions, i.e. “T” here indicates some adjustment to the torsion potential, but the precise nature of the adjustment depends on any other changes that have also been made to the standard OPLS-2005 force field. The final set of torsion parameter adjustments for each case is given in Table II. All torsional adjustments were made simply by varying the  $V_i$  parameters within the standard functional form for the OPLS torsion potential,

$$U(\omega) = \frac{1}{2}V_1(1 + \cos\omega) + \frac{1}{2}V_2(1 - \cos2\omega) \\ + \frac{1}{2}V_3(1 + \cos3\omega) + \frac{1}{2}V_4(1 - \cos4\omega),$$

where  $\omega$  is the torsion angle, and  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$  are the adjustable parameters.

### B. Bond-Stretching and Angle-Bending Adjustments

Results from ongoing work at Schrödinger to improve the OPLS force field indicate that bond stretching and angle bending restraints may be unrealistically stiff.<sup>17</sup> Indeed, we plotted the OPLS-2005 energy components for methyl-substituted stilbene and the two methyl-substituted bithiophenes, and the results indicate that angle bending and bond stretching energies both increase at very small torsion angles. As expected, the steric energy also increases at these angles, and, jointly, these trends suggest that this increased steric strain is distributed among different degrees of freedom, i.e., bonds are stretching and angles are bending in order to avoid costly steric clashes. If the constraints on these stretches and bends are too stiff, inappropriately high energies will result. Based on the observations at Schrödinger as well as our own investigations, we decreased the stretching and bending force constants by 30%, and minimized the stilbene and bithiophene derivatives according to this new potential. We also slightly increased the ideal values of two particular angles in the stilbene structures (those included in the  $\alpha$  dihedral, see Fig. 1), after visual comparisons of the OPLS-2005- and B3LYP-minimized

structures indicated that these angles were consistently smaller in the OPLS-2005 versions, bringing the rings into closer contact (see Methods for details).

We entitle this new potential “OPLS-SB-T,” and the corresponding results are represented in Figures 3 & 4 by a dotted orange line. The RMSD values between these OPLS-SB-T results and those from LMP2 are recorded in the third column of Table I.

*Stilbene Derivatives.* With these adjustments to the bond-stretching and angle-bending parameters, substantial improvements are obtained in the match between the OPLS-derived and LMP2-calculated  $\beta$  potential energy curves for all substituted stilbene derivatives, with an average improvement of 0.4 kcal/mol in the RMSD values as compared to the OPLS-T results. In addition, all but one of the OPLS-SB-T-derived  $\beta$  potential energy curves are within chemical accuracy, that is, within 1.0 kcal/mol of the LMP2-derived values. It is clear in Fig. 3e that the OPLS-SB-T potential results in marked improvements over both the OPLS-2005 and OPLS-T potentials. The one case that remains outside of chemical accuracy, with an RMSD value of 1.08, is that where  $R = OH$  (we discuss this case further in Section G).

*Bithiophene Derivatives.* Substantially more accurate results are obtained using the OPLS-SB-T potential for these molecules as well, with an impressive 0.6 kcal/mol average decrease in the RMSD between the LMP2 and OPLS-SB-T derived potential energy curves. The results for two bithiophene derivatives, 3,3'-diethyl-bithiophene and 3,3'-diisopropyl-bithiophene, remain outside of chemical accuracy. However, the decreases in RMSD for these two species were actually the most substantial in the set, with a decrease of 1.0 kcal/mol for the former and 1.2 kcal/mol for the latter.

Although the adjustments to OPLS-2005 described in this section are by no means a permanent solution, the improvements made by this simple heuristic approach are impressive. In addition, they are easily implemented, and can serve as a simple fix for such problems until the time when these stretching and bending force constants have been recalculated and reassigned in a more comprehensive fashion.

### C. Steric Repulsion Adjustments

The repulsive part of the standard 12-6 Lennard-Jones (LJ) potential has long been known to overestimate the repulsive forces at very short inter-atomic distances<sup>18,19</sup>. However, due to the ease of its calculation, this functional form has found its way into nearly all classical modeling potentials. Since biomolecular systems under reasonable temperatures and pressures do not often access the problematic region of the LJ potential, it is usually an acceptable approximation. However, as previously discussed, in conjugated polymers the joint effects of shorter bond lengths along the main chain and conjugation-induced planarity combine to force a small

Torsions	OPLS-2005	OPLS-T	OPLS-SB-T	OPLS-SB-B14-T
$\alpha$ angle				
??-CM-CM-??				
$V_1$	0.000	0.000	0.000	0.000
$V_2$	14.000	10.200	10.200	10.200
$V_3$	0.000	0.000	0.000	0.000
$V_4$	0.000	-1.200	-1.200	-1.200
$\beta$ angle				
CM-CM-CA-CA				
$V_1$	0.316	0.316	0.316	0.316
$V_2$	3.707	3.350	3.000	3.000
$V_3$	-0.974	-0.974	-0.947	-0.947
$V_4$	0.000	-0.100	-0.200	-0.200
$\gamma$ angles				
SA-CA-CA-CA				
$V_1$	0.276	0.276	0.276	0.276
$V_2$	1.234	1.234	1.234	1.234
$V_3$	0.376	0.376	0.376	0.376
$V_4$	0.000	-0.200	-0.200	-0.200
SA-CA-CA-SA				
$V_1$	1.241	1.241	1.241	1.241
$V_2$	-1.098	-1.098	-1.098	-1.098
$V_3$	0.681	0.681	0.681	0.681
$V_4$	0.000	0.200	0.200	0.200

TABLE II. Adjustments to the torsion parameter for the various OPLS potentials.

set of atoms into closer-than-usual contact.

Experimental deviations from the LJ 12-6 potential at short inter-particle distances have been well-documented for molecular hydrogen<sup>20</sup> as well as for the noble gases.<sup>21</sup> These deviations begin around  $0.8r_{\min}$ , where  $r_{\min}$  is the optimal inter-atomic distance in the standard LJ potential, and quickly become substantial as inter-atomic distances decrease further.<sup>20,21</sup> In our B3LYP-minimized structures, atoms of the substituted side-chains frequently come into closer than  $0.8r_{\min}$  contact with the atoms of the main chain in the near-planar configurations, suggesting that the LJ potential may be inadequate for these polymers.

We therefore consider the Buffered 14-7 potential, which, according to the analysis of experimentally-derived inter-atomic potentials for the noble gases, provides the best approximation of the true repulsive potential while keeping the attractive potential acceptably close to that described by the LJ function.<sup>21</sup>

The Buffered 14-7 potential can be written as

$$U(r) = \epsilon \left( \frac{1.07r_{\min}}{r + 0.07r_{\min}} \right)^7 \left( \frac{1.12r_{\min}^7}{r^7 + 0.12r_{\min}^7} - 2 \right),$$

where  $r_{\min}$  is the inter-atomic distance at which the potential is at its minimum, and  $\epsilon$  is the value at that minimum.

Results for this new potential, ‘‘OPLS-SB-B14-T,’’ are shown in Figures 3 & 4, indicated by a solid red line, and the RMSD values between these results and those from LMP2 are recorded in the last column of Table I.

As can be seen both in Table I and in Figures 3 & 4, the improvement to the potential energy curves resulting

from the use of the Buffered-14-7 potential is somewhat minimal. For the substituted stilbenes, its implementation actually worsens the match between the OPLS- and LMP2-derived potentials, albeit very slightly, with an average increase of 0.02 kcal/mol in RMSD as compared to that of the OPLS-SB-T potential. However, for the substituted bithiophenes, improvements in the match are seen in all cases, and there is an average decrease of 0.19 kcal/mol in the RMSD values. Although modest, the largest improvements occur in the near-planar configurations, where the LMP2- and OPLS-derived potentials deviate the most. As a result, we include this adjustment in our recommended potential, despite its modest effect. However, it should be noted that the same torsional adjustments are made to both the OPLS-SB-T and OPLS-SB-B14-T potentials, as shown in Table II, and can thus be used with either the Buffered 14-7 or the standard LJ potential.

## VII. OPLS-SB-B14-T-CALCULATED POTENTIALS

With the OPLS-SB-B14-T potential, we are able to reproduce, within chemical accuracy, the results of the LMP2 calculations for all except four of the the torsion potentials considered. The final average reduction in error between the LMP2- and the OPLS-derived potentials was 1.02 kcal/mol, and much of this reduction occurred in the low-angle region, precisely where the largest initial differences between the LMP2 and OPLS-2005 results were found. The four torsion potentials that deviate the

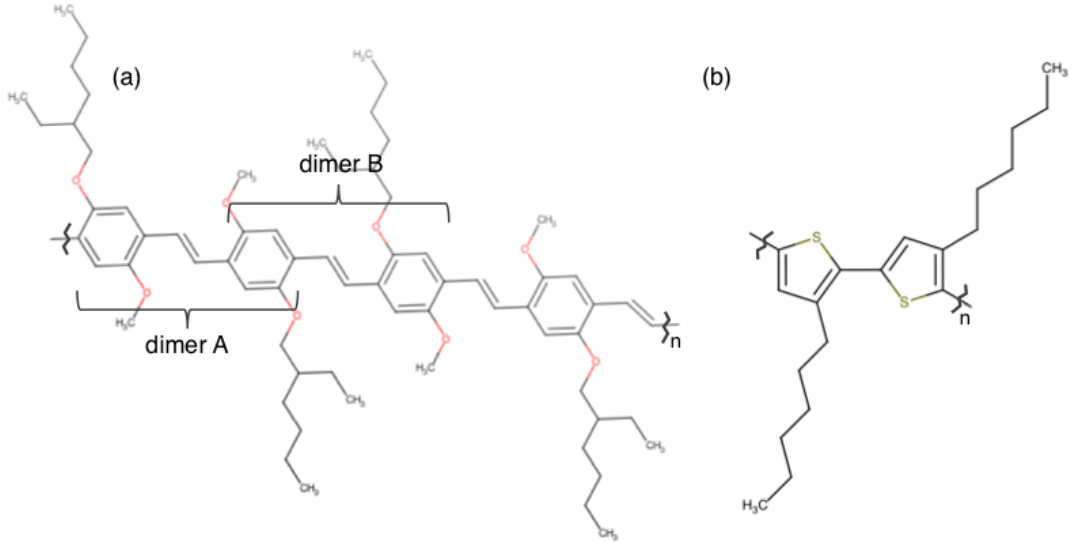


FIG. 5. The structures of (a) MEH-PPV and (b) P3HT. Note that there are two options for the side-chain configurations within an MEH-PPV dimer.

most from the LMP2 results when calculated with OPLS-SB-B14-T also had the largest deviations when calculated with OPLS-2005, and the final OPLS-SB-B14-T-derived RMSD values demonstrate significant improvements (see Table I). Importantly, the OPLS-optimized structures differ only minimally from the B3LYP-optimized ones with average structural RMSDs of 0.17 Å and 0.18 Å, when optimizing with OPLS-2005 and OPLS-SB-B14-T, respectively. (Averages were calculated over RMSDs for the 0°, 90°, and 180° structures of all torsions in Figures 3 & 4.)

The hydroxyl-substituted stilbene case deserves additional discussion. Compared to the curves of the other substituted stilbenes in Fig. 3, the  $R = \text{OH}$  case remains an outlier – both the barrier and the low-angle portion of the LMP2 curve are poorly reproduced by the OPLS-SB-B14-T potential. After close examination of the minimized structures, we hypothesize that the polar hydroxyl group may induce polarization to differing degrees as it rotates around the  $\beta$  dihedral angle. To test this hypothesis, we calculated the atomic charges from the electrostatic potential at the B3LYP/cc-pVQZ(-G) level. The results indicate that the charges on the hydrogens in the inter-ring linker region vary substantially with the  $\beta$  angle rotation. As the torsion approaches 0°, where the oxygen atoms of both OH groups are positioned close to one of the linker hydrogens, the charge on that hydrogen atom becomes more positive by about 60%, decreasing the energy of these low-angle conformations. Unfortunately, this kind of configuration-dependent polarization effect cannot be fully modeled within the limits of a non-polarizable potential.

## VIII. MD SIMULATIONS.

Using both the OPLS-2005 and the OPLS-SB-B14-T potentials, we performed MD simulations for polymers of P3HT (10 monomers in length) and MEH-PPV (60 monomers in length), two of the most widely studied conjugated polymers (see Fig. 5). We then examined the resulting trajectories for several features: their torsion angle distributions, persistence lengths, and conjugation length distributions. The lengths of the polymers investigated were intentionally chosen to approximate their persistence lengths. As a result, the polymers remained extended throughout the simulations, and complications arising from self-attraction and self-avoidance between disparate parts of the polymer were avoided. Additional simulation and analysis details can be found in the Methods section.

### A. Torsion Angle Distributions

Shifts in the distribution of sampled dihedral angles are clearly expected to result from the changes that differentiate OPLS-SB-B14-T from OPLS-2005, as these changes were designed to adjust the relative energies of these angles. Nevertheless, the distribution shifts for commonly-modeled polymers serve to illustrate the effect of these adjustments. The OPLS-2005 and OPLS-SB-B14-T potential energy curves for the  $\alpha$  and  $\beta$  torsions of MEH-PPV dimers and the  $\gamma$  torsion of the P3HT dimer are shown in Figure 6, while their sampled distributions during our MD simulations are shown in Figure 7.

As expected from the curves plotted in Fig. 6a, the distribution of sampled MEH-PPV  $\alpha$  angles broadens when

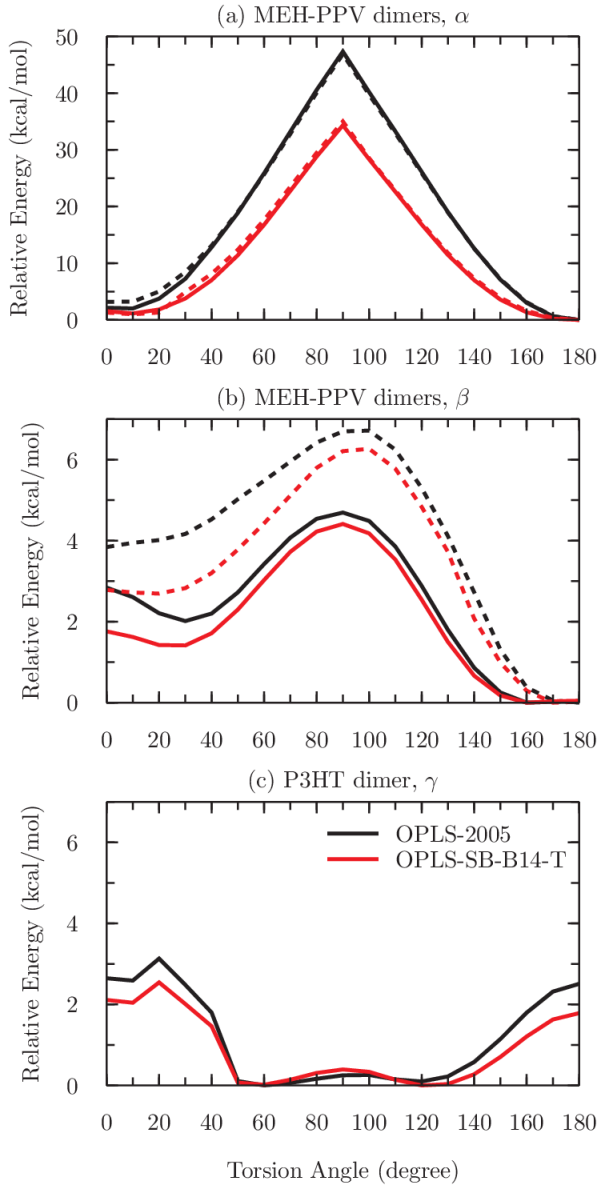


FIG. 6. The comparison between the OPLS-2005 and OPLS-SB-B14-T potentials for (a) the  $\alpha$  and (b) the  $\beta$  torsion angles of an MEH-PPV dimer, as well as (c) the  $\gamma$  torsion of a P3HT dimer. The solid lines in (a) & (b) represent the results for dimer A, while the dashed lines represent those for dimer B (see Fig. 5).

modeled with the OPLS-SB-B14-T potential. However the range of angles remains quite restricted, since the barrier between *cis* and *trans* configurations, although less than in OPLS-2005, remains greater than 30 kcal/mol. All  $\alpha$  dihedrals were initialized in the *trans* configuration, and the barrier appears insurmountable at our sampling temperature (295K). Similarly, the distribution of MEH-PPV  $\beta$  angles slightly broadens as expected with the use of the OPLS-SB-B14-T potential. Importantly, the population at small angles increases substantially over the

population that is present when modeled with OPLS-2005, demonstrating the conformational bias that results from an overestimation of the energy in this region, see Fig. 6b.

Finally, the distribution of P3HT  $\gamma$  angles also broadens with the implementation of OPLS-SB-B14-T. In this case, the likelihood of near-planar configurations with both large and small angles increases substantially. See Fig. 6c.

## B. Persistence Lengths

In modeling the behavior of long stretches of these polymers, it is important to properly represent their flexibility, especially when probing folding behaviors. We therefore calculated the persistence lengths of single, extended stretches of MEH-PPV and P3HT. The persistence length ( $L_p$ ) is the contour length over which correlations in the polymer's orientation persist (see Methods for details). Results indicate nearly identical persistence lengths for both OPLS-2005 and OPLS-SB-B14-T potentials.

For MEH-PPV, we calculated persistence lengths of  $53 \pm 4$  monomers using OPLS-2005 and  $51 \pm 2$  monomers using OPLS-SB-B14-T. Increased rotations around the  $\alpha$  torsion would be expected to result in a shorter  $L_p$ , but the slight broadening of values observed in the OPLS-SB-B14-T model (see Fig. 7a) appears insufficient to effect a statistically significant decrease in  $L_p$ . In contrast, changes to the rotations around the  $\beta$  angle are not expected to alter  $L_p$ ; since the bond to the adjacent monomer lies along the  $\beta$  torsion's rotational axis, the direction of the polymer does not meaningfully change with  $\beta$  angle rotations.

Experimental measurements of  $L_p$  range from 9 to 50 monomers for MEH-PPV.<sup>22–25</sup> However, the shorter-length values are derived from experiments on MEH-PPV polymers that most likely contained a substantial fraction of *cis* vinyl linkages and tetrahedral defects (where a single bond replaces the double bond in the vinyl group).<sup>22–24</sup> Depending on the synthetic method, *cis* and tetrahedral defects can each occur at up to 5% of the inter-phenyl linkages.<sup>26–29</sup> Since the persistence length is heavily influenced by such defects,<sup>24</sup> these shorter measurements are likely more reflective of the average distance between defects than the true stiffness of an all-*trans*, defect-free stretch of MEH-PPV. In contrast, the longest experimental estimate, 50 monomers,<sup>25,30</sup> is derived from vibrational spectra of individual stretching and bending modes in PPV, and thus provides a better estimate of its true stiffness (neglecting, however, the influence of the MEH side-chains). Its correspondence to our calculated  $L_p$  is striking.

For P3HT, the  $L_p$  was found to be  $8.8 \pm 0.9$  monomers using OPLS-2005 and  $8.7 \pm 0.4$  monomers using OPLS-SB-B14-T. The degree of rotation around the  $\gamma$  angle has a potentially significant effect on the persistence length,

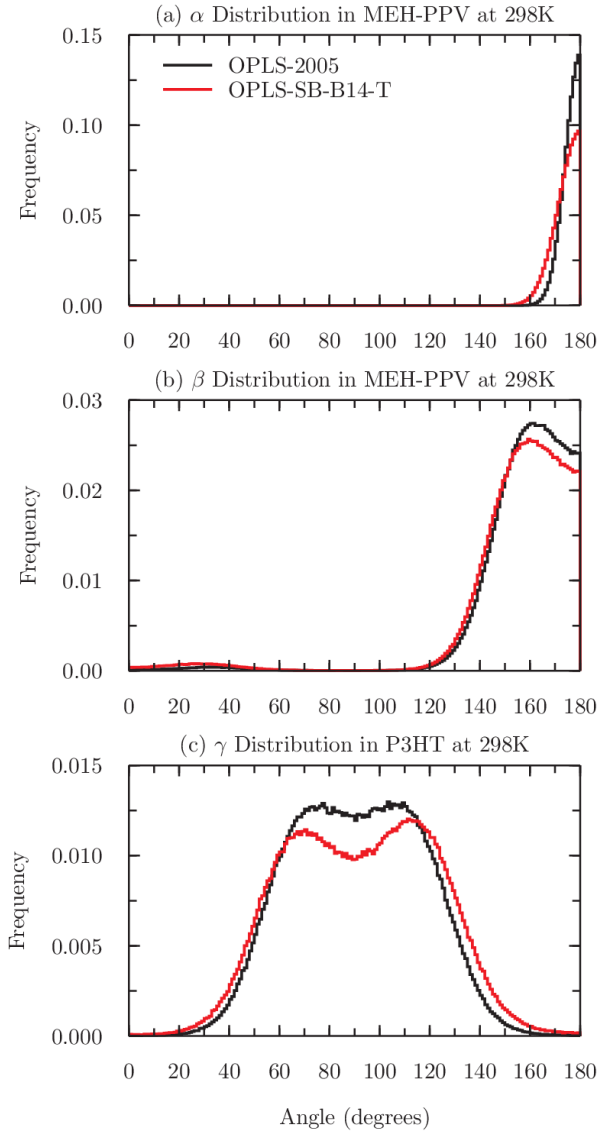


FIG. 7. Comparison of dihedral angle distributions from MD simulations using OPLS-2005 and OPLS-SB-B14-T for (a) the  $\alpha$  angle of MEH-PPV, (b) the  $\beta$  angle of MEH-PPV, and (c) the  $\gamma$  angle of P3HT.

especially if the near-planar configurations are heavily favored. However, these rotations access a wide-range of angles with both OPLS potentials, and therefore it is not surprising that we observe no change, especially given the shorter  $L_p$ . Experimental estimates of  $L_p$  for P3HT range from 6.2<sup>31</sup> to 8.6<sup>32</sup> monomers. As polythiophenes lack the kind of structural complications described above for PPVs, these measurements do represent the true polymer stiffness, and our calculated  $L_p$ , though slightly longer, is comparable.

### C. Conjugation Length Distributions

The conjugation length is the length over which the  $\pi$  electrons are delocalized in a conjugated system. Since a chromophore's electronic properties depend upon its length, understanding the distribution of conjugation lengths within a polymer is essential for understanding its behavior as a semi-conductor. Although the extent of potential conjugation, i.e. the length over which alternating single and double bonds extends, is sometimes used as a proxy for this conjugation length, the true conjugation length,  $L_c$ , can be shorter as a result of conformational variations that inhibit delocalization. In order for electrons to delocalize, p orbitals on the different atoms must be approximately coplanar, and thus rotations around conjugated bonds that break the planarity of the conjugated segment can also cause a break in conjugation. Rotations of greater than  $40^\circ$  from planarity have been found to induce changes in electronic properties,<sup>33</sup> and this cut-off has proven useful in estimating the extent of conjugation.<sup>34</sup> Using this metric, we calculated the distributions of conjugation lengths in MEH-PPV and P3HT during our MD simulations.

For MEH-PPV, the conjugation lengths in our simulations ranged from shorter than one monomer to the entire length of the 60-unit polymer, for both OPLS-2005 and OPLS-SB-B14-T potentials. Figure 8a shows the distribution of  $L_c$  values. With the adjustments included in OPLS-SB-B14-T, the distribution shifts towards shorter conjugation lengths and the average  $L_c$  is 5.6 monomers as compared to 7.2 monomers when the OPLS-2005 potential is used. We note, however, that in experiments with most MEH-PPV polymers, the presence of the tetrahedral and *cis* defects will impose additional limits on  $L_c$ .

For P3HT, very short conjugation lengths of just one monomer dominate the distributions, with average  $L_c$  values of 1.03 and 1.06 monomers for the OPLS-2005 and OPLS-SB-B14-T potentials, respectively. However, the dominance of one-monomer chromophores masks the substantial differences seen in the distributions of  $L_c$  values beyond this length, see Fig. 8b. In fact, the frequency of segments with a 2-monomer  $L_c$  doubles with the changes implemented in OPLS-SB-B14-T, while the frequency of conjugated segments extending for 3 or more monomers nearly quadruples.

It is important to note that for both MEH-PPV and P3HT, the self-association known to occur in condensed phases<sup>6,27</sup> will greatly influence the distributions of these conjugation lengths. Polythiophenes, in particular, are known to form extended crystals with nearly coplanar rings.<sup>6</sup> However, the additional forces present in the dense crystalline environment build upon the intrinsic inter-molecular forces, and it is clear from our analysis that even relatively small shifts in the dihedral angle distributions can have substantial effects when modeling the structural properties that influence electronic behavior.

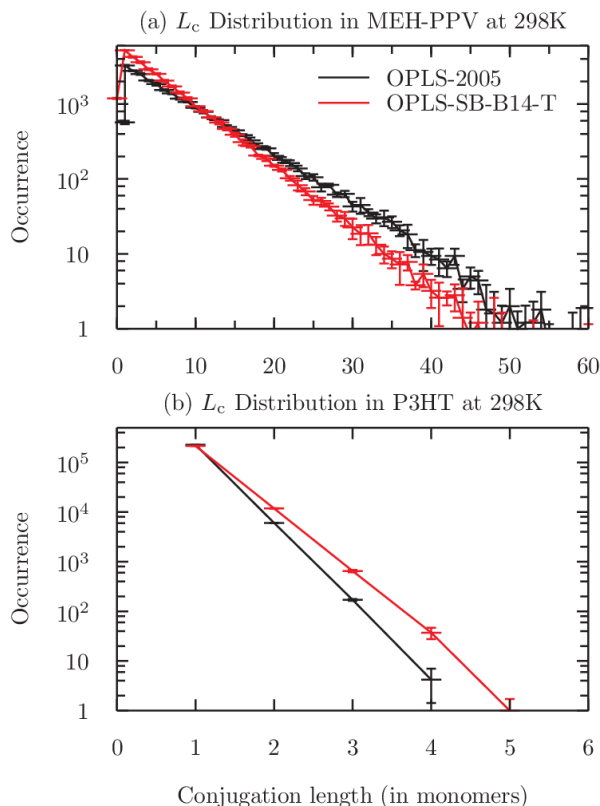


FIG. 8. Comparison of conjugation length distributions from MD simulations using OPLS-2005 and OPLS-SB-B14-T for (a) MEH-PPV, and (b) P3HT.

## IX. CONCLUSION

In this work, we have assessed the accuracy of a variety of classical force fields in modeling the constituents of PPV- and PT-based conjugated polymers. We then made adjustments to the OPLS-2005 force field in order to improve its modeling of the inter-ring torsion potentials of a series of substituted stilbene and bithiophene derivatives. Our new potential, OPLS-SB-B14-T, is based on the standard OPLS-2005 potential, but contains adjustments to the torsion, bond-stretching, and angle-bending parameters, while also utilizing the Buffered-14-7 potential to better approximate the steric repulsions at very close inter-atomic distances. These changes result in substantial improvements in the correspondence between the adjusted OPLS- and LMP2-derived torsional potential energy curves for two very different conjugated polymers with a variety of substituted side-chain groups. That these improvements were obtained for several different molecules with the same OPLS-SB-B14-T force field demonstrates this potential’s transferability and suggests that it should be applicable to other conjugated systems as well (although adjustments would have to be made to additional torsional parameters if the molecule contained main-chain dihedral angles other than those ad-

justed here). Our results also suggest that the corrections applied here may be necessary to appropriately model other systems where very short inter-atomic distances are encountered. Finally, we note that, with the exception of the Buffered 14-7 potential, the OPLS corrections proposed here require only simple adjustments to the OPLS parameter files. While work is underway at Schrödinger to provide a more comprehensive overhaul of these parameters for a wide range of conjugated moieties, the adjustments presented here allow us to more accurately explore the structural and electronic behaviors of PT- and PPV-based conjugated polymers.

Even very accurate classical force fields, however, will at some level prove inadequate at reproducing the forces acting within a given molecule, and in order to anticipate when and how the behavior of a modeled system will deviate from that of the physical one, we must understand of the types of errors expected. Our investigations of different substituent groups and a variety of force field variations have led us to an understanding of the types of errors that may be expected when using OPLS-like force fields to model these polymers (see Figures 3 & 4). In particular, we have learned that conformational change may significantly affect polarization in ways the OPLS-based potential is unable to replicate. Nevertheless, the improvements obtained with the OPLS-SB-B14-T potential enable us to more accurately model the energy basins and barriers of the inter-ring torsion potential, particularly for near-planar configurations, and to more accurately compare the behavior of polymers with different side-chains.

Our adjustments to the OPLS-2005 potential result in observable, if somewhat minor, shifts in dihedral angle populations during gas-phase MD simulations of P3HT and MEH-PPV. However these shifts did not translate into observable differences in persistence lengths. While these equilibrium properties may not look dramatically changed as a result of the OPLS modifications, barriers are substantially altered, as are the relative energies of planar and non-planar states. As a result, dynamical fluctuations will be sensitive to these more accurate potentials, and more substantial differences are to be expected in folding rates and excursions into higher energy configurations, such as fluctuations into and out of planar configurations. This last property is particularly important for understanding the electronic behavior of conjugated polymers, which depends heavily on these structural features. And, indeed, we do observe a far more substantial difference in the OPLS-2005 and OPLS-SB-B14-T calculated distributions of conjugation lengths (note the log scale on Fig. 8). An accurate modeling of these conjugation lengths is particularly important in techniques that couple quantum mechanical approaches to classical force fields in order to investigate excitations and charge transfer; such techniques may prove especially attractive in elucidating the functional properties of conjugated polymers.

Theoretical investigation into the semi-conducting na-



ture of conjugated polymer materials requires a multi-scale approach. Electron delocalization depends on molecular-scale details such as the degree of inter-ring twisting, while bulk transport efficiencies depend on polymer folding, aggregation, and the presence of grain boundaries between well-ordered regions. Appropriate modeling at the molecular level allows us to probe some of these features while facilitating the development of accurate coarse-grained models with which to probe longer times and larger systems.

## X. METHOD DETAILS

### A. QM Calculations

All geometries were optimized at the B3LYP/6-31+G\*\* level, followed by single-point calculations at the LMP2/cc-pVTZ(-f) level within Jaguar v. 7.6<sup>35</sup>. In stilbene, there are two symmetrically-equivalent  $\beta$  bonds. Therefore, in all geometry optimizations, one of these torsions was held at  $0^\circ$ , while the other was sampled at  $0^\circ, 10^\circ, \dots, 170^\circ, 180^\circ$ .

Electrostatic potential (ESP) single-point calculations were performed on all stilbene geometries with R=OH to test the effect of torsion on polarization of those geometries obtained at the B3LYP/6-31+G\*\* level. These calculations were performed using B3LYP at various basis sets (cc-pVDZ, cc-pVTZ, cc-pVQZ(-G)) to test for convergence of ESP with increasing size of the basis. Finally, the ESP calculated at the B3LYP/cc-pVQZ(-G) level were used to calculate the atomic charges.

### B. Molecular Mechanics Calculations

Starting with the QM-optimized geometries, structures were minimized using the OPLS-2005 potential as well as the OPLS-T, OPLS-SB-T, and OPLS-SB-B14-T potentials. As described above, torsions were sampled every  $10^\circ$  from  $0^\circ$  to  $180^\circ$ , and in stilbene, one  $\beta$  angle was held fixed at  $0^\circ$  while the other was rotated. Minimizations were performed using MacroModel<sup>14</sup> (for Fig. 2) and in-house Schrödinger software (for Figs. 3, 4, & 6) with no interaction cutoffs and the dielectric constant set to 1.0. We used the  $10^\circ$  B3LYP-minimized structure as the initial configuration for the OPLS-minimization of 3,4'-dimethyl-bithiophene structures at  $0^\circ$ , as the  $0^\circ$  B3LYP-minimized structure appeared to be caught in a false minimum on the OPLS potential energy surface. In addition, we restrained four dihedral angles within the long, floppy side-chains of the MEH-PPV and P3HT dimers in order to obtain a smooth potential. The restrained dihedral angles were chosen so that the side-chains remained pointed out into space and therefore did not clash during rotation. Since LMP2-minimized structures were unavailable for these dimers, optimizations were begun from structures that had been previously optimized with OPLS-

2005. The MM3\* potential used in Fig. 2 differs slightly from that of MM3 as derived by Allinger and coworkers<sup>9</sup> in that it uses partial charges instead of bond dipoles, improper torsions for out-of-plane bending, and specific, static, torsional terms for conjugated systems without an iterative SCF bond order calculation.<sup>14</sup>

*Torsion Adjustments.* Incremental adjustments were made manually to the  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$  torsion parameters until a good match was obtained to the QM-derived curves for unsubstituted stilbene (for the  $\alpha$  and  $\beta$  angles) and for unsubstituted bithiophene (for the  $\gamma$  angle). Adjustments for the OPLS-SB-T and OPLS-SB-B14-T potentials were made as the last step after all other adjustments. Table II shows the final values of these parameters for each potential.

*Bond-Stretching and Angle-Bending Adjustments.* A small increase was made to the ideal value of the CA-CM-CM angle, where CA and CM are atoms types within OPLS. (This angle is included in the  $\alpha$  dihedral, see Fig. 1), from  $123.66^\circ$  to  $128.30^\circ$ . In addition, all stretching and bending force constants were reduced by 30%. These adjustments were motivated by our comparisons of the QM-minimized and OPLS-2005-minimized structures as well as by preliminary results at Schrödinger. The specific values were chosen after investigations demonstrated their utility in improving the resulting match to the QM-derived potential energy curves.

*Steric Repulsion Adjustments.* The Buffered 14-7 potential was introduced instead of the LJ 12-6 potential based on previous work demonstrating that it more accurately approximates the steric repulsions between noble gases at very short inter-atomic distances.<sup>21</sup> Several other adjustments to the repulsive part of the LJ potential were also tested, but only those that resulted in an unacceptably soft potential appeared to substantially improve to the match to the QM results. It is important to note that the  $r_{\min}/\sigma$  ratio is 0.18% larger for the Buffered 14-7 than the LJ 12-6. We used the same  $\sigma$  values for both potentials, and the  $r_{\min}$  values are computed accordingly.

*Comparisons to QM potentials.* Comparisons were made between the LMP2- and the OPLS-derived potential energy curves through the use of visual inspection (see Figs. 3 & 4) and RMSD quantification (see Table I).

### C. MD Simulations

MD simulations of P3HT and MEH-PPV polymers were run using both OPLS-2005 and OPLS-SB-B14-T within TINKER.<sup>36</sup> The P3HT molecules were 10 monomers in length and regio-regular, with all head-to-tail linkages (as represented by the 3,4'-disubstituted bithiophenes). The MEH-PPV molecules were 60 monomers in length, with regio-regular, syndiotactic side-chain placement. Polymer lengths were chosen so that the polymers remained extended throughout the simulations in order to avoid complications from self-attractions

and self-avoidance in our measured quantities.

OPLS-2005 and OPLS-SB-B14-T parameter input files were created for TINKER with the use of in-house Schrödinger software. Sampling was done within the NVT ensemble at 298K, using the velocity verlet algorithm with 2 fs timesteps and an Andersen thermostat. A dielectric constant of 1.0 was used, and tapered cutoffs were implemented from 10.8 to 12.0 Å for the van der Waals attractions and from 7.8 to 12.0 Å for the electrostatic interactions. Although truncating the electrostatic potential always results in the loss of a significant portion of the electrostatic energy, we observed that the effect of this cutoff on the differences in energy between various polymer configurations was minimal – even smaller, in fact, than the effect of introducing periodic boundary conditions and using Ewald summation to approximate the long-range electrostatic contributions. Thus it appears that, for our purposes of comparing energies between identical polymers in various extended configurations, implementing such a cutoff in the electrostatic potential is acceptable. Previous simulations on conjugated polymers also make use of this approximation.<sup>6</sup>

Five trials of P3HT were run for 120 ns each, with atomic positions collected for analysis every 5 ps. For MEH-PPV, twenty-five trials were run for 6 ns each, and atomic positions were collected every 10 ps. All runs started from different extended configurations generated during an equilibration run. Each set of simulations was run twice, once using OPLS-2005 and once using OPLS-SB-B14-T.

*Calculations of  $L_p$ .* Persistence lengths were determined by fitting the decay in polymer orientation to the following relation:

$$\langle \cos \theta_{i,i+j} \rangle = \exp(-S_j/L_p) \quad (1)$$

where  $\theta_{i,i+j}$  is the angle between vectors tangent to the polymer at monomers  $i$  and  $i+j$ ,  $S_j$  is the contour length between monomers  $i$  and  $i+j$ , and  $L_p$  is the persistence length. Tangent vectors were defined as running from the start of one monomer to the start of the next.  $j$  was varied from 0 to 9 monomer units for P3HT and 0 to 10 for MEH-PPV. Multiple points were collected

from each polymer configuration, i.e. the averaging of  $\cos \theta$  ran both over different configurations as well as over different  $i$  positions. For P3HT, the persistence length was fit separately for each MD trial, and the average and standard deviation values were calculated across these five trials. For MEH-PPV, the persistence length was fit separately for five groups, each of which included data from five independent MD runs, and the average and standard deviation values were calculated across these five groups.

*Calculations of Dihedral Angle Distributions.* Dihedral angles were collected from all output configurations from all runs, binned in 1° increments, and plotted in Figure 7.

*Calculations of  $L_p$ .* Conjugation lengths were determined by measuring the dihedral angles between moieties that would ideally be coplanar when conjugated. For P3HT, only  $\gamma$  was considered. (See Figure 1b.) For MEH-PPV, three angles were considered: two  $\beta$  and  $\alpha$ . (See Figure 1a.) Conjugation lengths were then gathered from all configurations and binned in 1 monomer increments (with each of the three angles in MEH-PPV contributing an appropriate fraction of a monomer). Histograms were calculated separately for the five trials of P3HT and the five groups of five trials each for MEH-PPV so that error bars could be determined for the histogram values. Figure 8 presents these averaged histograms.

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