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# Torsional Barriers and Correlations between Dihedrals in *p*-Polyphenyls

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The torsional energy curves for biphenyl, *p*-terphenyl, and *p*-quaterphenyl are calculated using the B3LYP density functional with a triple-$\zeta$ polarized basis set. In agreement with recent accurate literature data, barriers of similar height are found at 0° and 90° for biphenyl. For the higher members, the torsional energy curves show an increasing tendency to lower the barrier of the coplanar conformations. The correlation effects between different dihedrals are reasonably small and discussed extensively. In addition, torsional potential functions at different levels of accuracy, suitable for computer simulations, are proposed for all the members of the series up to *p*-quinquephenyl.

## 1. Introduction

The series of *p*-polyphenyls certainly exhibits fascinating properties in the fields of polymers and liquid crystals. In the former, the applications of poly(*p*-phenylene) vary from ribbons and fibers to solid-state lubrificants, and the polymer itself has been the object of several reviews.[1] In addition, *p*-quinquephenyl and *p*-sexiphenyl show nematic and smectic phases respectively, whereas the smallest member of the series, the biphenyl molecule, can be seen as a "building block" for the rigid core of many mesogenic molecules. Moreover, the biphenyl molecule has been the object of many studies, both experimental[2−5] (see also references in refs 6 and 7) and theoretical.[6−13] Of particular interest is the delicate interplay between intermolecular and intramolecular forces that drives the phase transitions. Indeed, the angle between the two rings is around 40° in the gas phase,[3−5] and 32° in the liquid phase,[14] while the molecule is found in a nearly planar conformation in the crystalline phase.[2] The tendency for the torsional angle to increase with temperature is apparent also in the larger homologues,[15] where the molecular planarity is lost on going from the crystalline to less ordered structures.

Computer simulations appear to be a useful tool for understanding this molecular behavior, provided suitable force fields are available for both inter- and intramolecular interactions. In particular, an accurate description of the torsional potential energy in the regions far from the minimum is crucial in the condensed phase, where the intermolecular potential can induce less favorable torsional conformations. In addition, quantum effects are expected to be small for the torsional motion; consequently, classical molecular dynamics appears be adequate.

In a recent molecular dynamics simulation study[12] of the biphenyl molecule, torsional motion was described by a potential function proposed by Tsuzuki et al.,[6] obtained by interpolating ab initio data at the MP4(SDQ)/6-31G*//HF/6-31G* level. Semiempirical potentials were also used[8,9] to achieve an understanding of the interplay between inter- and intramolecular forces in the crystal structure. However, both of these potentials show large disagreements with the experimental measures: gas-phase data[3−5] result in similar barrier heights between 1.4 and 1.6 kcal/mol in the planar and 90° conformations, whereas ref 6 accounts for 3.47 and 1.58 kcal/mol and ref 8 for 2.15 and 3.57 kcal/mol, respectively. However, as pointed out in ref 16, the experimental estimates of the barriers are obtained by extrapolation of the potential energy function and are affected by a large uncertainty (±0.5 kcal/mol).

Recently, torsional energy barriers of biphenyl have been calculated[7] with different quantum-mechanical methods: the authors found that density functional calculations yield results closer to the experimental data, while MP2 methods fail to give a good description of the near-planar region, where they predict a too high relative energy. This overestimation of the 0° barrier was ascribed to an underestimation of the correlation energy, which is expected to be enhanced at 0° by the $\pi$ conjugation between the two rings. However, those authors did not consider a nearly contemporary paper by Tsuzuki et al.,[16] who demonstrated that MP2, coupled with a very extended basis set, is able to predict the correct torsional barriers. Thus, it appears that both MP2 and DFT can give correct results for torsional energy calculations, the former being much more basis set demanding.

In this work we aim to produce a simple torsional potential function for the *p*-polyphenyl series, suitable for computer simulations. For this purpose we take into account the correlation between adjacent torsional angles, and, to simplify the resulting potential energy function, we consider accurately the errors arising from a complete decoupling of their contribution to the electronic energy.

In the next section we describe the method used for the calculation of the curves and the details of the fitting procedure. The results obtained are discussed in section 3, while conclusions are drawn in section 4.

## 2. Method

In all calculations the well-tested density functional B3LYP method,[17] with a triple-$\zeta$ polarized basis set 6-311G(2d,p), was employed. During the geometry optimizations, no symmetry restriction was imposed except for the torsional angles. In

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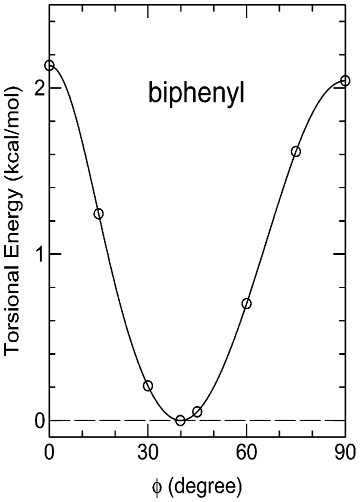

**Figure 1.** Torsional energy for biphenyl. The DFT data (circles) and interpolated torsional potential $F(\phi)$ (solid line) are reported.

**TABLE 1: Electronic Energies ($\Delta E_e$) for Some Selected Values of the Torsional Angle $\phi$ of Biphenyl**[a]

| $\phi$ (deg) | $\Delta E_e$ (kcal/mol) | $\Delta E_{ZPE}$ (kcal/mol) | ref 7 $\Delta E_e$ (kcal/mol) | ref 15 $\Delta E_e$ (kcal/mol) |
|---|---|---|---|---|
| 0 | 2.14 | 0.03 | 2.17 | 2.28 |
| 39.9 | 0.00 | 0.00 | 0.00[b] | 0.00[c] |
| 90 | 2.04 | −0.12 | 1.88 | 2.13 |

[a] In the third column the computed zero-point correction $\Delta E_{ZPE}$ is reported. The energies of ref 7 are corrected by ZPE. All energies are scaled with respect to the absolute minimum. [b] BPW91/6-31+(d) calculations; energy minimum at 40.35°. [c] MP2/cc-PVQZ results; energy minimum at 45.0°.

contrast, the absolute energy minimum was obtained by a complete geometry optimization. Since in all cases all of the aromatic rings remain practically planar, the torsional angles can be defined as the angle between two adjacent rings. All calculations were performed with the GAUSSIAN 98 package.[18] For terphenyl, for which no literature data are available, an MP2 calculation was also carried out in order to validate the present DFT results. The resulting energy curves vs the torsional dihedrals were then represented by suitable expansion onto trigonometric functions whose linear parameters were determined by a least-squares fitting.

The zero-point energy (ZPE) was computed at the same level of accuracy for geometries corresponding to absolute energy minima or maxima, where null first derivatives allow a harmonic treatment of the vibrational eigenvalue problem. For consistency, the torsional frequency (which is imaginary at the maxima) was never included in the ZPE. Owing to the small coupling between the torsional internal coordinate and the other normal vibrational modes, this can be done to a high level of accuracy.

## 3. Results and Discussion

**3.1. Biphenyl.** The torsional energy curve for the biphenyl molecule is reported in Figure 1. In Table 1, energy values for angles corresponding to energy extrema are reported, together with other theoretical estimates. All energy values are scaled with respect to the absolute energy minimum, which is found at 39.9°. The two maxima at 0° and 90°, accounting for 2.14 and 2.04 kcal/mol, respectively, are almost symmetrical and are in close agreement with recent DFT results that include the ZPE.[7] The results of Tsuzuki et al. at the MP2 level[16] using a large basis set are also reported for comparison: they yield similar barriers but a larger torsional angle. With respect to the experimental estimate, our theoretical results predict slightly higher barriers.

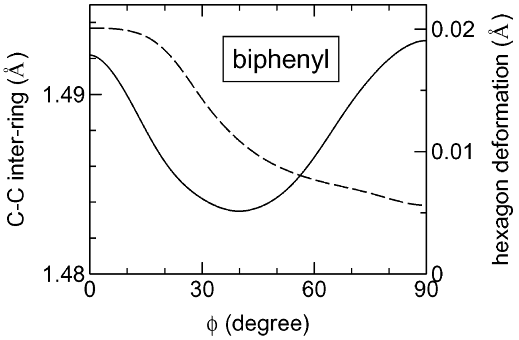

**Figure 2.** Ring−ring distance in biphenyl (full line, left scale) and the hexagonal deformation index (dashed line, right scale) versus the torsional angle.

As is well known,[7,16] the torsional barriers are determined by the competition between the steric repulsion between the ortho neighboring hydrogens belonging to different rings, which is minimized when the two rings are orthogonal, and the stabilization arising from the inter-ring $\pi$-conjugation, which is enhanced in the planar conformation. This is expected to increase the vibrational frequencies involving the H nuclei which approach each other in the planar conformation. Indeed, as shown in Table 1, the ZPE is maximum in the planar geometry and presents a minimum in the 90° conformation, where the distance between such hydrogens is large.

From qualitative considerations it is expected that the torsional angle is correlated with the distance between the two rings, i.e., the distance between the two bonded carbon atoms of different rings. This is demonstrated by Figure 2, which shows that this C−C distance is always intermediate between the typical values of the aromatic C−C bond, 1.39 Å, and the aliphatic C−C bond, 1.54 Å. In the planar conformation the C−C distance is increased by the steric repulsion between hydrogens, whereas at 90° the lack of conjugation shifts the bond distance toward the single bond value. Thus, the minimum value is found near the more stable conformation, where some inter-ring conjugation is still expected. Another quantity strongly correlated with $\phi$ is the hexagonal deformation index (HDI, see Appendix), which expresses the deviation of both the carbon and the hydrogen skeletons from a regular planar hexagon. From Figure 2, it appears that this quantity is always very small but shows a clear monotonic trend toward a perfect polygon as the torsional angle increases. The value of the HDI at the equilibrium geometry—about twice the minimum—accounts for the interplay between conjugation and distortion effects arising from the repulsion of the ortho hydrogens.

During all optimizations, no significant deviation from planarity was observed in both phenyl rings. Nevertheless, geometry optimization is important, as the energy gain deriving from geometry relaxation is not negligible. For example, the planar energy barrier obtained by a rigid motion of the equilibrium conformer ($\phi = 39.9°$) is found to be 0.58 kcal/mol higher than the relaxed one.

An analytical torsional potential function $F(\phi)$ can be obtained by a least-squares fitting using Fourier expansion:

$$F(\phi) = \sum_{n=0}^{N} C_n \cos(2n\phi) \tag{1}$$

with $N$ ranging from 4 to 7. The coefficient values of the $N = 7$ and $N = 4$ fittings are reported in Table 2. The accuracy of

**TABLE 2: Parameters from the Fitting of the Torsional Potential of Biphenyl**[a]

| $n$ | $C_n$ ($N = 7$) | $C_n$ ($N = 4$) |
|---|---|---|
| 0 | 0.984834 | 1.003626 |
| 1 | −0.175215 | −0.155120 |
| 2 | 1.005707 | 1.002066 |
| 3 | 0.181207 | 0.186577 |
| 4 | 0.083866 | |
| 5 | 0.039487 | |
| 6 | 0.015021 | |
| $\sigma$ | 0.003 | 0.070 |
| MAE | 0.006 | 0.130 |

[a] All coefficients $C_n$, standard deviations $\sigma$, and MAE are in kcal/mol.

**TABLE 3: Barrier Heights as a Function of the Two Torsional Angles of *p*-Terphenyl**

| $\phi_1$ (deg) | $\phi_2$ (deg) | $\Delta E_0$ (kcal/mol) | $\Delta E_{\mathrm{ZPE}}$ (kcal/mol) |
|---|---|---|---|
| 0 | 0 | 3.81 | −0.06 |
| 0 | 90 | 4.23 | −0.17 |
| 38.4 | −38.4 | 0.00 | 0.00 |
| 90 | 90 | 4.28 | −0.31 |

the fitting procedures was estimated by means of both the standard deviation, $\sigma = (\chi^2)^{1/2}$, and the maximum absolute error (MAE). The second fitting is given here to provide a less expensive torsional potential to be used in bulk simulations where its accuracy can be considered satisfactory.

**3.2. *p*-Terphenyl.** The main question about the torsional potential energy of the *p*-terphenyl molecule concerns the dependence of the total energy on the two internal dihedrals $\phi_1$ and $\phi_2$. Are they coupled in same way, or does the rotational energy result from independent contributions of $\phi_1$ and $\phi_2$? Electronic energy curves were first calculated at torsional angles $\phi_1$ and $\phi_2$ by a 15° step, allowing optimization of all the other internal coordinates. Also in this case, the two vibrational frequencies ascribable to torsional motion were not included in ZPE. The absolute minimum was found at $\phi_1 = -\phi_2 = 38.4°$, i.e., with the first and the last phenyl rings lying in the same plane. The local minimum in the helix conformation ($\phi_1 = \phi_2 = 38.4°$) differs from this value by 0.008 kcal/mol, a quantity comparable with the level of accuracy of the geometry optimization and surely smaller than the level of accuracy of the electronic calculation. Therefore, the helix and non-helix conformations were considered degenerate in the following discussion.

Energy barriers of about 4 kcal/mol were found in the coplanar (0−0), in the 0−90, and in the 90−90 conformations. These data are reported in Table 3, together with the corresponding relative ZPEs which, according to the previous discussion on biphenyl, show a maximum in nearly coplanar conformations due to the repulsion between ortho hydrogen atoms.

In contrast to the case with biphenyl, the lowest barrier height is found in the planar conformation. This indicates that the $\pi$ conjugation is more effective for three coplanar rings. Indeed, the energy gain from the 90−90 to the 0−90 is only 0.05 kcal/mol, whereas a further ring conjugation relaxes the energy by 0.4 kcal/mol. Also, the value of $\phi_1 = -\phi_2$ at the equilibrium geometry (1.5° lower than that of biphenyl) may be considered a consequence of the effectiveness of the three-ring conjugation.

To get a deeper insight, the energy barriers of terphenyl can be analyzed in terms of those of biphenyl by summing the contribution of the two dihedrals using the barriers of biphenyl. We obtain 4.28, 4.23, and 4.08 kcal/mol respectively for the 0−0, 0−90, and 90−90 conformations, with errors of 0.47, −0.05, and −0.20 kcal/mol. The smallest error is in the 0−90 conformation, while in the coplanar conformation both geometry rearrangements and three-ring conjugation effects make the barrier height rather indistinguishable from that of biphenyl.

Since no other data exist in the literature for *p*-terphenyl and the barrier heights are sensitive to both the level of theory and the basis set, it would be desirable to compare our results with those obtained by MP2, which has been widely used for the evaluation of such quantities. Therefore, we performed MP2 calculations with the same basis set 6-311G(2d,p) at the geometries reported in Table 3, obtained by DFT calculations. Since for this type of calculation the convergence of MP2 relative energies with basis set is rather slow,[16] a more extended basis set should be employed to obtain accurate results. Nevertheless, this is the largest basis set which our computer can bear for this molecule, and we believe the MP2 results can furnish useful information on the reliability of the DFT torsional profiles.

The obtained MP2 barriers were 5.24, 4.86, and 4.18 kcal/mol for the 0−0, 0−90, and 90−90 conformations, respectively. These values are to be compared with the DFT values 3.81, 4.23, and 4.28 kcal/mol reported in Table 3. A marked disagreement is apparent: the MP2 barriers tend to favor the perpendicular geometries, with a large overestimate (≃1.6 kcal/mol) for the 0−0 conformer. This trend is in line with the results for biphenyl reported by Tsuzuki et al.,[16] who studied the convergence of the MP2 energy barriers with basis set. For the 0 and 90 conformations, they found 2.88 and 1.74 kcal/mol, respectively, by using the cc-pVDZ basis set, which is comparable with the 6-311G(2d,p) one. When the almost complete cc-pVQZ basis was used, these values moved to 2.28 and 2.13 kcal/mol, respectively, showing an overestimate of 0.6 kcal/mol for the planar conformation and an underestimate of 0.4 kcal/mol for the perpendicular conformation; these errors are ascribable to the incompleteness of the basis set. It is worth noticing that DFT calculations with moderate basis sets agree with the latter in giving comparable barrier heights of about 2.1 kcal/mol.[7] Thus it appears that, with moderate basis sets, the MP2 energies tend to favor the conformations with small inter-ring conjugation, where the absolute value of the correlation energy $E_c$ is expected to be smaller. A simple rationale may be found by supposing that the fraction of correlation energy given by MP2, with moderate basis sets, is almost independent of the torsional angle. In this case we can expect an overestimate of the energy proportional to $E_c$, which results in an unbalanced MP2 energy for varying torsional angle.

For terphenyl these features are expected to be even more marked. Since it is reasonable to suppose that $E_c(0-0) > E_c(0-90) \simeq E_c(\mathrm{equil}) > E_c(90-90)$ (confirmed both by DFT and MP2 results), it follows that MP2 energies may give an overestimate for the 0−0 barrier and an underestimate for the 90−90 barrier. This is just what we observe with respect to the DFT results, which, by these arguments, appear more reliable than the present MP2 ones.

Moreover, it is seen that both MP2 and DFT results indicate that the three-ring conjugation is very effective in stabilizing the 0−0 conformation. In fact, the MP2 barrier height increases by 0.68 kcal/mol on going from the 90−90 to 0−90 conformations and only by 0.38 kcal/mol in the second step toward the planar conformation. The difference between these two values (−0.30 kcal/mol) can be ascribed to the three-ring conjugation. The fact that a similar value (−0.37 kcal/mol) is found in the

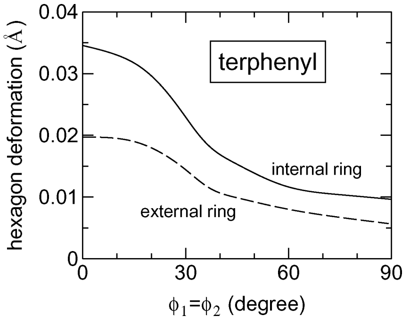

**Figure 3.** Hexagonal deformation index for the rings of terphenyl versus the torsional angles, which are kept equal.

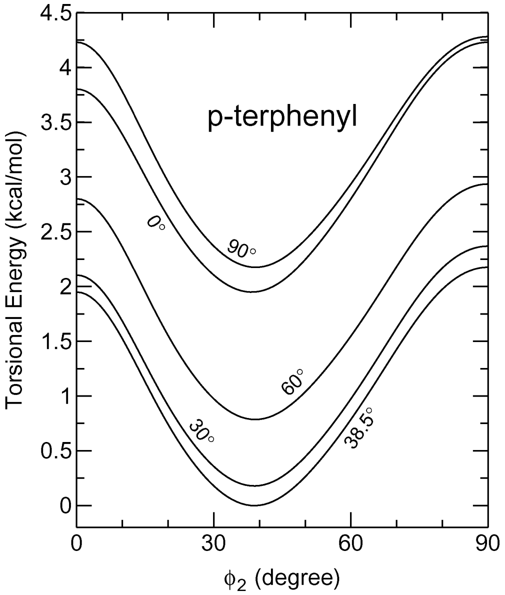

**Figure 4.** Torsional energy for *p*-terphenyl. The internal torsional potential is given as a function of the dihedral $\phi_2$, with $\phi_1$ fixed at the reported value.

DFT results reinforces the validity of the DFT method for studying the effects of conjugation in polyphenyls.

The HDIs of the external and internal rings of terphenyl are reported in Figure 3, obtained by varying a torsional angle. To simplify the analysis, the other dihedral is taken as equal to the first one. The trend of the HDIs for the two external rings is similar to that of biphenyl, whereas the internal rings always show larger distortions. Even for $\phi_1 = \phi_2 = 90°$, the HDI is higher for the internal ring because of the double substitution of hydrogen with phenyl versus a single substitution for the external rings. At lower angles the distortion is due mainly to the hydrogen shell rather than to the carbon shell. The capability of the former to deviate from the hexagonal shape while preserving conjugation allows the molecule to gain a fraction of a kilocalorie per mole in energy, to make the 0−0 barrier the lowest one.

It is apparent that the computed energy curves, some of which are reported in Figure 4, differ from each other for a nearly constant energy shift. This suggests that the correlation between dihedrals should be small, and it is expected that the two-dimensional torsional energy can be written to a reasonable level of accuracy as a sum of independent contributions of $\phi_1$ and $\phi_2$. However, coupling between the two torsional angles can be estimated quantitatively from fitting procedures. For this purpose the computed energies have been fitted with the function

$$G(\phi_1,\phi_2) = (F(\phi_1) + F(\phi_2))(1 + H(\phi_1,\phi_2)) \qquad (2)$$

**TABLE 4: Parameters for the Fitting of the Torsional Potential of *p*-Terphenyl at Three Levels of Approximation**[a]

| *n,m* | $C_{n(m)}$ | $C_n$ | $C_n$ |
|---|---|---|---|
| 0 | 0.996012 | 0.996035 | 1.010594 |
| 1 | −0.312048 | −0.312739 | −0.301796 |
| 2 | 0.981185 | 0.980621 | 0.990701 |
| 3 | 0.169688 | 0.169421 | 0.169183 |
| 4 | 0.078231 | 0.078039 | |
| 5 | 0.034780 | 0.034691 | |
| 6 | 0.014515 | 0.014505 | |
| 1,1 | −0.023901 | | |
| 1,2 | −0.004578 | | |
| 2,1 | −0.004578 | | |
| 2,2 | −0.001588 | | |
| $\sigma$ | 0.010 | 0.047 | 0.106 |
| MAE | 0.028 | 0.112 | 0.283 |

[a] The coefficients $C_{nm}$, $\sigma$, and MAE are in kcal/mol.

**TABLE 5: Barrier Heights as a Function of the Three Torsional Angles of *p*-Quaterphenyl**

| $\phi_1$ (deg) | $\phi_2$ (deg) | $\phi_3$ (deg) | $\Delta E_0$ (kcal/mol) |
|---|---|---|---|
| 38.4 | −36.8 | 38.3 | 0.00 |
| 0 | 0 | 0 | 5.46 |
| 0 | 0 | 90 | 5.92 |
| 0 | 90 | 0 | 6.44 |
| 0 | 90 | 90 | 6.48 |
| 90 | 0 | 90 | 6.34 |
| 90 | 90 | 90 | 6.54 |

where *F* has the form of eq 1 and $H(\phi_1,\phi_2)$ accounts for the correlation between the dihedrals and is given by

$$H(\phi_1,\phi_2) = \sum_{n=1}^{M}\sum_{m=1}^{M} C_{nm}\cos(2n\phi_1)\cos(2m\phi_2) \qquad (3)$$

As can be seen from Table 4, all coefficients $C_{nm}$ are small, and the torsional potential of *p*-terphenyl molecule can be expressed, to a good level of accuracy, as a sum of two independent functions, each referred to a decoupled dihedral. In this case, the MAE of 0.11 kcal/mol (next-to-last column of Table 4) can be considered as an upper bound of the error arising from neglecting correlation between dihedrals. Nevertheless, its accuracy is adequate for most molecular simulations. However, an even more simplified expansion, using only four terms, is reported in the last column of Table 4. Apparently, the values for the highest $C_n$ coefficients do not differ much from the ones obtained for biphenyl. However, using the $C_n$ of biphenyl to reproduce the energy of terphenyl, we obtain $\sigma = 0.25$ and MAE $= 0.46$; the latter is found in the planar conformation.

**3.3. *p*-Quaterphenyl.** In view of the computational effort required for the calculation of *p*-quaterphenyl, a small number of geometrical points were considered. The computed energy barriers for given $\phi_1$, $\phi_2$, and $\phi_3$ equal to 0° and/or 90° are reported in Table 5.

With respect to biphenyl and terphenyl, the computed equilibrium dihedrals are slightly lower. The value of $\phi_2$ (about 1.5° lower than $\phi_1$ and $\phi_3$) seems to underline the importance of the ring position for the conjugation effects. Indeed, the tendency to assume coplanar conformations appears to be more effective for the internal rings. As for terphenyl, and in line with this observation, the lowest barrier is found for the coplanar conformation, with a net energy gain of more than 1 kcal/mol with respect to the 90−90−90 one, which is the most unfavored. The trend of the coplanar energy barrier is appreciated by considering that the 0−0 barrier of biphenyl times 3 is 6.42 kcal/mol and the 0−0−0 barrier of terphenyl multiplied by 3/2 is 5.72 kcal/mol, versus a real value of 5.46 kcal/mol. This is

**TABLE 6: Parameters for the Fitting of the Torsional Potential of Quaterphenyl**[a]

| *n,m* | $C_i$ | $D_i$ | $C_i$ | $D_i$ |
|---|---|---|---|---|
| 0 | 1.02635 | 1.08201 | 0.99384 | 1.14476 |
| 1 | −0.35994 | −0.27183 | −0.38419 | −0.20293 |
| 2 | 0.92569 | 1.17289 | 0.91135 | 1.20570 |
| 3 | 0.21757 | −0.06133 | 0.23785 | −0.10032 |
| 1,1 | | | −0.01643 | |
| $\sigma$ | 0.110 | | 0.056 | |
| MAE | 0.24 | | 0.10 | |

[a] All coefficients $C_i$, $D_i$, standard deviations $\sigma$, and MAE are in kcal/mol.

probably also due to the value of the dihedral at the equilibrium geometry: 39.9°, 38.4°, and 37.6° (averaged) for bi-, ter-, and quaterphenyl, respectively. This systematic decrease makes the equilibrium conformation somehow more and more similar to the coplanar one.

The lower barrier of the 0−0−90 geometry with respect to the 90−90−90 (≃0.5 kcal/mol) is consistent with the difference between the 0−0 and the 90−90 barriers in terphenyl. The difference of ≃0.5 kcal/mol between the 0−0−90 (three coplanar rings) and 0−90−0 (two pairs of coplanar rings) barriers confirms the particular stability of three (or more) consecutive coplanar rings. All in all it appears clearly that, on going toward longer *p*-polyphenyls, the conjugation effects are able to partially overcome the repulsion between ortho hydrogens, and smaller dihedrals are energetically favored.

The small correlation between the dihedrals of the *p*-terphenyl molecule suggests that the internal rotational potential $F_n(\phi_1,\phi_2, ..., \phi_{n-1})$ of any *p*-polyphenyl can be expressed as a simple sum of $n - 1$ identical potential functions, each depending on one angle. Unfortunately, it was verified that this approximation led to large errors, at least for *p*-quaterphenyl. A more realistic approximation has to account for the internal and external dihedrals. Thus, we have fitted the computed energies with the function

$$F_n(\phi_1,\phi_2, ..., \phi_{n-1}) = \sum_{i=0}^{N} C_i[\cos(2i\phi_1) + \cos(2i\phi_{n-1})] + \sum_{i=0}^{N} D_i \sum_{k=2}^{n-2} \cos(2i\phi_k) \quad (4)$$

with $n = 4$ in the present case. The results are reported in the second and third columns of Table 6.

It is evident that the MAE of 0.24 kcal/mol, found in conformations in which at least one angle is 90°, is not very satisfactory; however, attempts to extend the expansion (4) does not give sensible improvements. The inclusion of a minimal correlation function

$$F_4(\phi_1,\phi_2,\phi_3) = \left(\sum_{i=0}^{N} C_i[\cos(2i\phi_1) + \cos(2i\phi_3)] + \sum_{i=0}^{N} D_i \cos(2i\phi_2)\right) \times (1 + C_{1,1} \cos(2\phi_1)(2\phi_2) + C_{1,1} \cos(2\phi_2)(2\phi_3)) \quad (5)$$

leads instead to a net lowering of both $\sigma$ and MAE (fourth and fifth columns of Table 6).

Thus, from the results of both ter- and quaterphenyl, it appears that the energy contribution ascribable to correlation effects should not exceed 0.2 kcal/mol.

**3.4. Test of the Potential: *p*-Quinquephenyl.** Since the computational effort required for the calculation of *p*-quinquephenyl is very high, we consider now only the equilibrium geometry and the coplanar conformation. The four torsional angles at the equilibrium geometry of *p*-quinquephenyl are very similar to those of quaterphenyl. This indicates that the increasing effect of the multiring $\pi$ conjugation, on going from biphenyl to quaterphenyl, reaches somehow a sort of convergence for the higher members of the series.

To test the accuracy of the Fourier expansion determined for quaterphenyl in reproducing the torsional energy of quinquephenyl, the energy barrier of the all-coplanar (0−0−0−0) geometry was computed. The choice of this geometry was driven by the important role it plays in the condensed phase.[15] The Fourier energy barrier, computed by using eq 4 with $N = 4$ and $n = 5$, was 7.38 kcal/mol, while by including the correlation by eq 5 we obtain 7.08 kcal/mol. These values are to be compared with the DFT value of 7.10 kcal/mol. The accuracy of the first estimate is excellent, whereas neglecting correlation leads to an error comparable with those already discussed for ter- and quaterphenyl.

## 4. Conclusions

We have presented a B3LYP/6-311G(2d,p) calculation of the torsional energy the *p*-*n*-phenyl series up to $n = 5$ with the aims of obtaining information about the geometrical structure and of providing useful data to be subsequently employed to model the internal degrees of freedom in bulk computer simulation. Particular attention has been devoted to the all-coplanar conformations which experimentalists have supposed to be populated in condensed phases.

In agreement with other recent theoretical estimates, the present calculations on biphenyl predict torsional barriers at 0° and 90° close to each other and in accord with experimental data. In contrast, for terphenyl, the coplanar conformation appears to give the lowest barrier. This trend is more and more marked on going toward the higher members of the series and has been interpreted as the result of the interplay between repulsion among ortho hydrogens and multiring conjugation effects. Evidently, the latter are capable of driving dihedrals at the equilibrium geometry to slightly lower values and of stabilizing the coplanar conformation with respect to those where two adjacent rings lie on orthogonal planes. The coplanar energy barriers of 3.8 and 5.5 kcal/mol for terphenyl and quaterphenyl, corresponding to $6k_BT$ and $9k_BT$, respectively, do not rule out the possibility that the intermolecular forces can induce planar conformation in condensed phases. This will be verified in future work, where the present torsional energy as well as ab initio intermolecular forces[19] will be employed in computer simulation.

## 5. Appendix

Let us suppose that the *xy* plain contains an aromatic ring or a sequence of atoms placed near the vertices of a regular polygon. In the case of a not perfect planarity, the *xy* plane is the least-squares plane. The polygon deformation index (PDI) is defined as the square root of $\chi^2$,

$$\mathrm{PDI} = \sqrt{\chi^2} \quad (6)$$

with

$$\chi^2 = \frac{1}{n}\sum_{j=1}^{n}\left[X_j - X_0 - R\cos\left(\frac{2\pi j}{n} + \varphi\right)\right]^2 + \left[Y_j - Y_0 - R\sin\left(\frac{2\pi j}{n} + \varphi\right)\right]^2 + Z_j^{\,2} \quad (7)$$

where $X_0$, $Y_0$, $R$, and $\varphi$ are adjustable parameters whose meaning should be evident. $n$ is the number of atoms and the number of sides of the polygon. Once the four parameters are optimized by minimizing $\chi^2$, PDI represents a sort of standard deviation of the polygon, drawn by the considered atoms with respect to a perfect one. In the case of a number of atoms less than the number of sides, the above expression has to be slightly modified. The argument of the cosine and sine functions is to be modified according to the orientation of the $(X_j,Y_j)$ vector in a straightforward manner. For the present cases, $\chi^2$ is computed by including in the sum both the C and the H atoms belonging to the ring and optimizing the five parameters $X_0$, $Y_0$, $R_C$, $R_H$, and $\varphi$.

## References and Notes

(1) Kovacic, P.; Jones M. B. *Chem. Rev.* **1987**, *87*, 357.

(2) Delugeard, Y.; Charbonneau, G. P. *Acta Crystallogr. B* **1976**, *33*, 1586.

(3) Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S.; Almenningen, A. *J. Mol. Struct.* **1985**, *128*, 59.

(4) Bastiansen, O.; Samdal S. *J. Mol. Struct.* **1985**, *128*, 115.

(5) Wise, W. B.; Kurland, R. J. *J. Am. Chem. Soc.* **1964**, *86*, 1877.

(6) Tsuzuki S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 139.

(7) Goeller, A.; Grummt, U. *Chem. Phys. Lett.* **2000**, *321*, 399.

(8) Baranyai A.; Welberry, T. R. *Mol. Phys.* **1991**, *73*, 1317.

(9) Baranyai A.; Welberry, T. R. *Mol. Phys.* **1992**, *75*, 867.

(10) Chakrabarti, A.; Yashonath, S.; Rao, C. N. R. *Mol. Phys.* **1995**, *84*, 49.

(11) Celebre, G.; De Luca, G.; Longeri, M.; Catalano, D.; Veracini, C. A.; Emsley, J. W. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2623.

(12) Palke, W. E.; Catalano, D.; Celebre, G.; Emsley, J. W. *J. Chem. Phys.* **1996**, *105*, 7026.

(13) Cheung, D. L.; Clark, S. J.; Wilson, M. R. *Phys. Rev. E* **2002**, *65*, 051709.

(14) Steele, D.; Eaton, V. J. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 1601.

(15) Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. *Polym. Pap.* **1993**, *34*, 1571.

(16) Tsuzuki, S.; Uchimaru, T.; Matsamura K.; Mikami M.; Tanabe, K. *J. Chem. Phys.* **1999**, *110*, 2858.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1.; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Amovilli, C.; Cacelli, I.; Campanile, S.; Prampolini G. *J. Chem. Phys.* **2002**, *117*, 3003.