Stiffer under strain: mechanical properties of poly-*p*-phenylene

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The mechanical properties of poly-*p*-phenylene and its simplest oligomer, biphenyl, have been explored by *ab initio* and semiempirical molecular orbital methods. The contribution of zero-point energy to the torsional barrier is negligible, but the variation of vibrational entropy with torsion increases the height of the free energy barriers to rotation through the D_{2h} and D_{2d} conformations. The computed Hessians argue for a backbone that becomes 14% stiffer when strained to planarity. Cluster calculations of the polymer using periodic boundary conditions illuminate the role of bowing in compression and the importance of intermolecular forces to compressive mechanical performance of rigid-rod polymers.

(Keywords: mechanical properties; poly-*p*-phenylene; biphenyl)

INTRODUCTION

The mechanical properties of conjugated polymers may be superior to those of their saturated counterparts due to intrachain π-bonding. At the same time, bulk properties of rigid-rod polymers are clearly influenced by intermolecular forces which are conveniently analysed with molecular dynamics simulations and empirical force fields[1]. Empirical force fields are derived from fewer observables than degrees of freedom, so closer scrutiny of small molecules using molecular orbital methods provides complementary insight into the mechanical properties of polymers. As part of a continuing study of the microscopic basis for mechanical strength, we consider the electronic structure of poly-*p*-phenylene (PPP) and its simplest oligomer, biphenyl[2–5]. The experimental dihedral angle of the phenyl rings (*Figure 1*) in biphenyl decreases from 45° in the gas phase to 32° in the melt and 10° when crystalline. These observations imply that the magnitude of the torsional potential is similar to potentials imposed by intermolecular packing forces in liquids and crystals.

PPP is among the simplest of the rigid-rod polymers, which are so named because rotation about the σ-bonds between rings causes no change in chain length[6]. Our primary objective is to assess the response of the PPP chain to tension and compression. For the simplest oligomer, biphenyl, we employ *ab initio* methods to examine the role of vibrational zero-point energy and entropy at the D_{2h}, D_2 and D_{2d} stationary points on the Hartree–Fock (HF) potential energy surface. The molecular response to stress is then calculated from the inverse of the HF Hessian matrix at each stationary point. Finally, we compute the properties of a polymer chain using a semiempirical molecular orbital method and periodic boundary conditions.

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COMPUTATIONAL TECHNIQUE

Geometry optimization in D_{2h}, D_2 and D_{2d} symmetry were performed using Cadpac issue 4.0 on a Cray XMP computer[7]. Initial Restricted Hartree Fock (RHF) geometry optimizations with a gradient tolerance of 10^{-5} and a 3-21G basis were repeated with the 6-31G** basis to verify that the stationary points were basis independent.

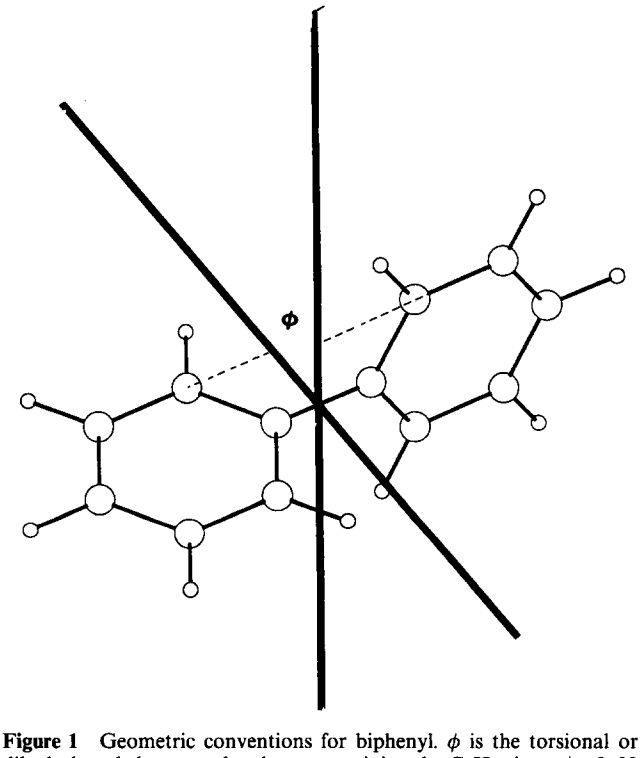

Figure 1 Geometric conventions for biphenyl. ϕ is the torsional or dihedral angle between the planes containing the C_6H_5 rings. $\phi = 0$, 39 and 90° correspond to the stationary points in D_{2h}, D_2 and D_{2d} symmetry according to the HF/6-31g** calculations

The HF/3-21G second derivative or Hessian matrix

$$\mathscr{H}_{ij}=\frac{\partial^2 E}{\partial R_i \partial R_j}$$

was used both for vibrational frequency analysis and computation of the molecular response to stress.

Molecular moduli were computed for an arbitrary force vector $\vec{F}$, whose elements specify the Cartesian components of the forces applied to each atom in the molecule:

$$\mathscr{H}\vec{R}=\vec{F}$$

$\vec{F}$ is then left multiplied by the inverse of the Hessian to yield the virtual displacements $\vec{R}$ of each atom in the cluster[8]:

$$\vec{R}=\mathscr{H}^{-1}\vec{F}$$

The projection of the virtual displacements along the direction of stress, $\vec{j}$, is converted to a modulus ε with reference to the equilibrium length (L) and the cross-sectional area σ:

$$\varepsilon=\frac{|\vec{F}|L}{|\vec{R}\cdot\vec{j}|\sigma}$$

We have recently applied this method to anisotropic stress in C_{60} (ref. 9).

Semi-empirical calculations employed MOPAC version 5.0[10] with the Austin Model 1 (AM1)[11] and PM3[12] parametrized Hamiltonians. Optimization of the D_2 biphenyl was performed without constraints, while a single constraint on the dihedral angle was used for the D_{2h} and D_{2d} cases.

Polymer calculations used a cluster model with periodic boundary conditions[13] and the AM1 Hamiltonian, as we have previously reported for polyethylene[2]. Full optimizations with up to four phenyl rings in the unit cell were performed to verify size-extensivity of the enthalpy and length per phenyl ring. Constrained optimizations were accomplished by fixing the length of the translation vector, which defines the connection between translationally equivalent atoms. This corresponds to a fixed uniaxial strain.

RESULTS

Biphenyl torsion

The most stable conformation of biphenyl has a dihedral angle of 39° and faces a larger barrier to rotation through the planar geometry than through the D_{2d} form. The nuclear coordinates describing the stationary points are virtually unchanged on moving from 3-21G to 6-31g** bases, though second derivative calculations with the larger basis were computationally prohibitive. The C–H bonds are slightly elongated, and the optimum value of ϕ shifts less than 1° with the larger basis. Total energies at this level are about 2.6 hartrees lower (*Tables 1* and *2*), suggesting that one is not at the HF limit, perhaps complicating interpretation of Möller Plesset perturbation theory estimates of the correlation energy[14]. The contributions of electron correlation at the MP4(SDQ)/6-31G*//HF/6-31G* level of theory, which raises both barriers by less than 1 kJ mol^{-1}, have been explored elsewhere[15].

Proper description of the torsion requires consideration of the zero-point and entropic contributions to the Gibbs free energy. Second derivative calculations at each of the stationary points yield one imaginary frequency each for the D_{2d} ($78i$ cm^{-1}) and D_{2h} ($46i$ cm^{-1}) conformations. The contributions of zero-point vibrational energy (0.5 $\sum_i h\nu_i = 511$ kJ mol^{-1}) differ by less than 50 cm^{-1} at each stationary point, so that the energy and enthalpy barriers are equally high.

The vibrational entropy, $S_v(T)$, can be estimated from the computed frequency spectra at each geometry:

$$S_v(T)=k_B \ln\left(\prod_i \frac{1}{1-\exp^{-h\nu_i/k_B T}}\right)$$

We treat the two imaginary frequency modes as free rotors ($S\approx k_B/2=4.16$ J mol^{-1} K^{-1}). At 300 K the Gibbs free energy, $G=H-TS$, is lower than the enthalpy by 7.75, 10.97 and 9.13 kJ mol^{-1} for the D_{2h}, D_2 and D_{2d} conformations, respectively. The free-energy barriers at 0 and 90° are thus respectively 1.84 and 3.21 kJ mol^{-1} higher than their enthalpic counterparts.

The AM1 torsional enthalpy variations in *Figure 2* show an asymmetric barrier, as found with *ab initio* methods. However, its PM3 counterpart is qualitatively inconsistent with the *ab initio* results, and is unphysical given the available experimental data on biphenyl. This qualitative shift in predicted torsional potential on moving to the *newer* parametrization provides another cautionary note on the application of semiempirical methods to estimation of force fields[16].

There are recent reports that the semiempirical

Table 2 Summary of energetics for the D_{2d}, D_{2h} and D_2 conformations of biphenyl

Method	ΔE_0 (kJ mol^{-1})	ΔE_{90} (kJ mol^{-1})	E_{scf} (Hartrees)	ϕ (deg)
HF/321G	16.33	3.65	−457.6887	39
HF/6-31g**	13.72	6.11	−460.2716	39
TS 300 K	3.23	1.84		
AM1	8.7	4.21		43
PM3	−2.1	2.0		50

Table 1 Summary of *ab initio* HF twist angles (ϕ) and energy barriers at the planar (ΔE_0) and D_{2d} (ΔE_{90} geometries)

ϕ (deg)	ΔE_0 (kJ mol^{-1})	ΔE_{90} (kJ mol^{-1})	Method	Ref.
32	5.0	18.9	Hybrid LCAO	32
39	8.6	10.0	STO-3G	33
44	13.0	9.0	STO-3G	39
45	13.5	6.9	HF/6-31G	38
46	13.9	6.3	MP4(SDQ)/6-31G*//HF/6-31G*	15

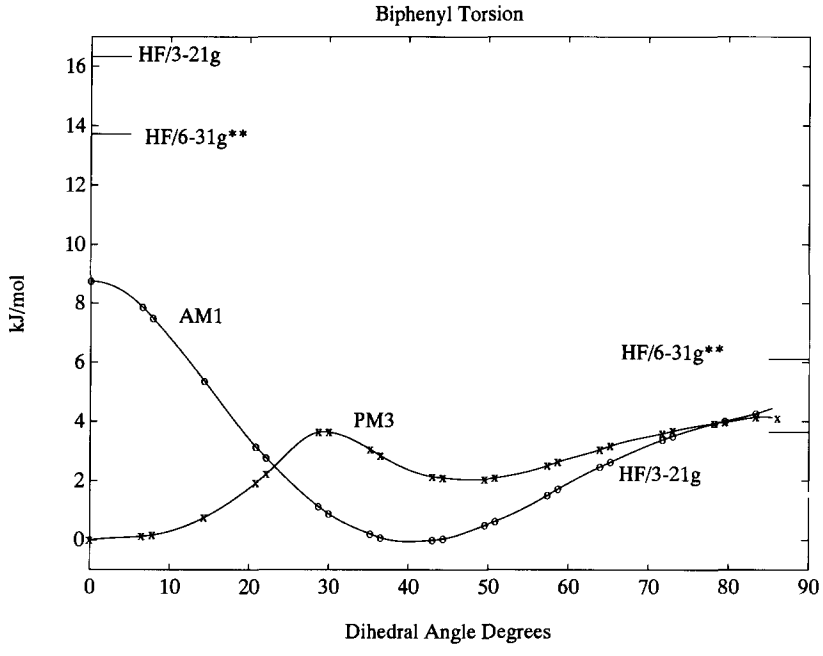

Figure 2 Semiempirical potentials for torsional motion about the inter-ring bond obtained by fixing only the dihedral angle and performing optimizations at each conformation. AM1 (×) and PM3 (○) results are accompanied by spline fits (——). Also shown are the barrier heights at 0 and 90° computed with the *ab initio* techniques

methods yield accurate vibrational spectra[17,18]. The root-mean-square variations of the vibrational spectra on distortion from D_2 to D_{2d} and D_{2h} are 87 and 2.2 cm^{-1} with the AM1 Hamiltonian. The *ab initio* results show root-mean-square changes of 79 and 172 cm^{-1}. Both methods predict similar changes on twisting ϕ to 90°. However, changes to the spectrum on moving to the planar conformation are substantially greater in the *ab initio* results.

BIPHENYL STIFFNESS

The D_2 and D_{2d} conformations become more coplanar in response to uniaxial stress. In other words ϕ decreases with tension. The stiffness or molecular modulus of these conformations is identical, 183 ± 3 GPa. Virtual displacements caused by the same force on the planar D_{2h} conformation show no torsional motion and a modulus of 211 GPa, which is 14% higher than the twisted conformations.

These molecular moduli assume that the cross-sectional area is unchanged by strain. In a real solid, more efficient packing of either conformation would increase the Young's modulus since the area, σ, appears in the denominator of the expression for ε.

Polymer stiffness

The enthalpy per C_6H_4 group, 105 ± 1 kJ mol^{-1} in the primitive unit cell, is the same for the optimized geometries with two, three and four rings in the cell. The length per C_6H_4 unit, 4.29 Å, is also independent of the size of the unit cluster. These results are reflected in *Figure 3*, which presents the computed enthalpies and unit cell dimensions per phenyl unit using the AM1, semiempirical Hamiltonian. As the size of the unit cell increases, the number of $\vec{k}$ points in the first Brillouin zone over which the electronic energy is averaged also increases[19]. Stability of the optimized enthalpy and geometry with changing unit cell size implies that the contribution of dispersion in the band structure to the total electronic energy is minimal.

While the calculations are size-extensive for the total energy and geometry, there is a shift in the calculated stiffness with the size of the unit cell. *Figure 3* shows the variation of enthalpy with strain for the constrained optimizations using two, three, and four C_6H_4 rings per unit cell. The shapes of the curves in tension are indistinguishable, and geometric changes show a gradual decrease in the average value of ϕ with strain. In compression we find chain moduli near zero while $dH/d\Delta$ decreases as the size of the unit cell increases. This qualitatively different behaviour is a consequence of bending by the rigid rod, as illustrated in *Figure 4*.

The second derivatives of the potentials in *Figure 3* yield moduli of 460, 340 and 360 GPa for the two-, three- and four-ring unit cells, respectively. The error associated with numerical fitting is about 25 GPa. The optimization algorithm does not guarantee global minimization, since the unit cell size is incremented in small (0.03 Å) steps. Thus it is possible that the softer compressive behaviour for the $n=3$ calculations is a consequence of the qualitatively different geometry illustrated in *Figure 4*.

DISCUSSION

Biphenyl torsion

Experiments on biphenyl in the gas[20–23], liquid[24], solution[25–28] and solid[29–31] phases all support a non-planar, D_2 geometry where ϕ, the torsional or dihedral angle between the planes of the phenyl rings, is sensitive to the local environment (*Figure 1*). The molecule has also been repeatedly studied using electronic structure techniques with the aim of describing this torsional potential[15,32–34]. Biphenyl provides a textbook illustration of the interplay between resonance stabilization of the planar D_{2h} geometry and steric repulsion of the *ortho* hydrogens, which favours a

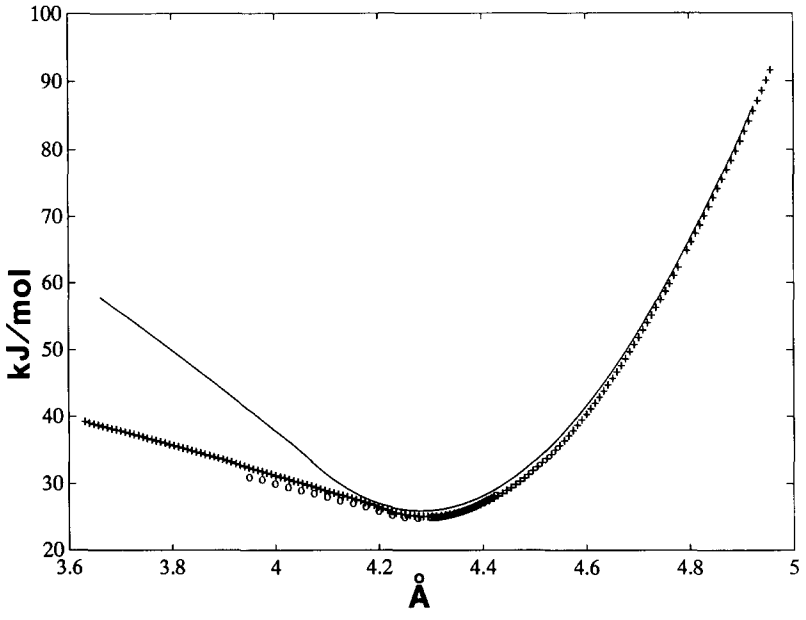

Figure 3 Changes of enthalpy (kJ mol^{-1}) with strain (Å) for PPP with two (−), three (+), and four (○) C_6H_4 rings per unit cell. Enthalpies, lengths and strains are per phenyl ring, so that variations represent behaviour that is not size-extensive

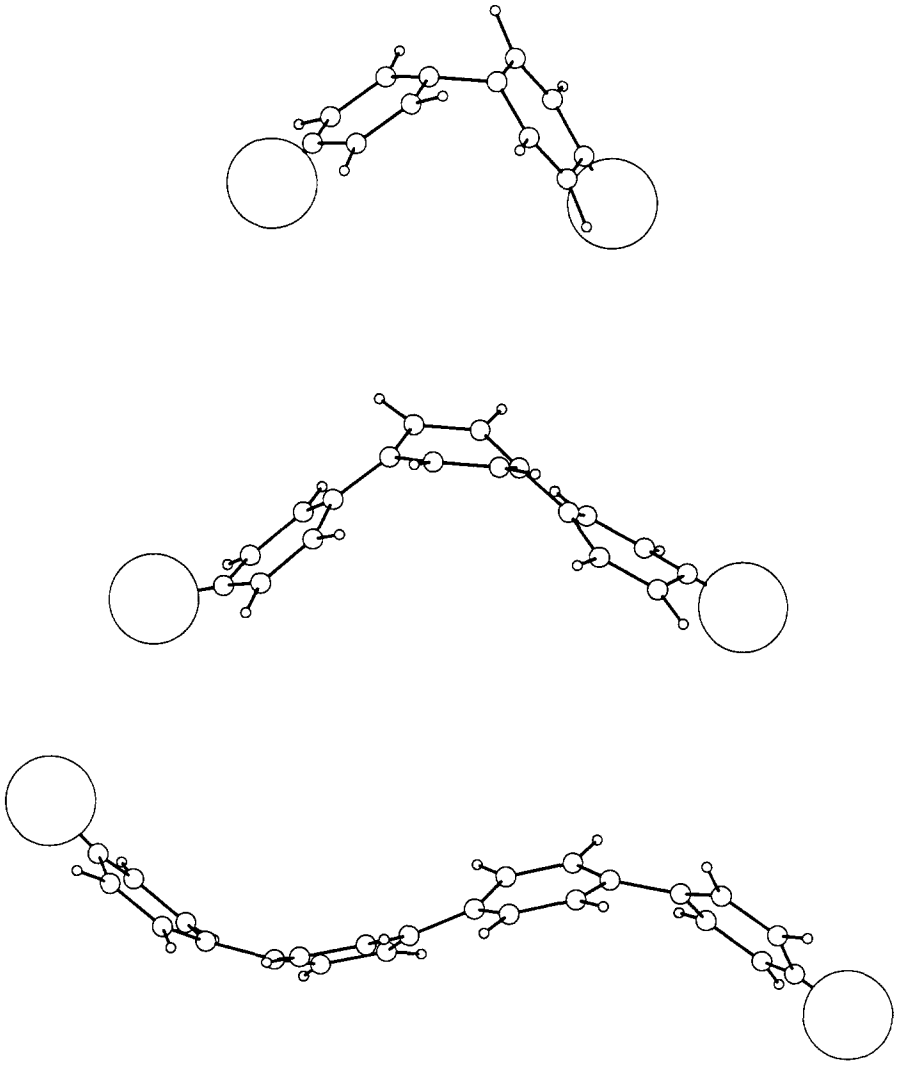

Figure 4 Compressed geometries for two, three and four C_6H_4 rings per unit cell at approximately 1% strain. The compressive strength of the $n=3$ model is substantially less than the $n=2$ and $n=4$ cases

perpendicular D_{2d} conformation[35]. The dihedral angle is a sensitive probe of intermolecular interactions in crystals and solutions, as their magnitude is comparable to that of the torsional potential.

Electron diffraction data have been used to measure the geometry and torsional potentials for a variety of substituted gaseous biphenyls[20,23]. The results imply that $\phi = 44.4 \pm 1.2°$, which agrees with the present results obtained using *ab initio* and AM1 Hamiltonians. The electron diffraction data are mute on the magnitudes of torsional barriers at D_{2h} and D_{2d} symmetry, as are data obtained by analysis of the Raman overtone spectra[28].

The dihedral angle is reduced to $32.3 \pm 2°$ in the molten state as well as in solution, based on the infra-red spectra of isotopically substituted biphenyls[24]. A recent examination of the proton magnetic resonance spectrum of biphenyl in a nematic liquid crystal solvent finds an angle of $34 \pm 1°$, in accord with molten and dissolved phases[26].

Neutron diffraction from $C_{12}D_{10}$ implies that $\phi = 10°$ in the solid state[31]. A systematic survey of 101 crystal structures containing biphenyl moieties has shown that packing forces in the solid state drive ϕ to near 0°, and also induce librational motion, which offsets the formal steric repulsion of the *ortho* hydrogens[36]. Similar results have been reported from crystallography of PPP oligomers with six, seven and eight phenyl rings[1].

Already in 1945 there was interest in understanding the theoretical basis for biphenyl's torsional dynamics based on benzene molecular orbitals[37]. Previous computational work on biphenyl includes extended Huckel, neglect of differential overlap (CNDO, INDO), Parriser–Parr–Pople molecular mechanics and *ab initio* efforts which are nicely summarized by Hafelinger and Regelmann[38]. The predicted dihedral angle varies from 25 to 45°, with the exception of the CNDO calculations which predict a D_{2d} geometry[34]. In one STO-3G analysis of biphenyl[33], the lowest energy form had a dihedral angle of 38.6° and barriers at 0 and 90° of 8.59 and 10.04 kJ mol^{-1}, respectively. This optimization was performed while constraining the phenyl rings to be planar. The second such study[39] relaxed this constraint and reported an equilibrium dihedral angle of 43.8° and potential barriers at 0 and 90° of 13 and 9 kJ mol^{-1}, respectively. Thus the highest calculated barrier moved from D_{2d} to D_{2h} symmetry. More elaborate calculations have since been reported, which optimize the geometries using larger, polarized basis sets and perturbation theory estimates of the correlation energy[15].

It has been known since 1973[24] that the frequency spectrum of biphenyl is sensitive to the torsional angle. It is therefore possible that changes in the molecular stiffness would alter the zero-point energies of the rotational conformations. As ϕ increases from zero, the symmetry shifts from $D_{2h} \rightarrow D_2 \rightarrow D_{2d}$, a saddle-point mode disappears and reappears, coupling of the ring π-electrons changes, and the *ortho* hydrogens experience different steric environments. Both *ab initio* and semiempirical methods show frequency shifts with torsion; however, the zero-point contribution to the enthalpy is no different for the three conformations. Vibration does influence the energetics of torsion through changes of the vibrational entropy with dihedral angle. As the saddle points are approached, one mode is softened but the remaining modes are stiffened, so that the vibrational entropy decreases away from the equilibrium conformation. In the case of biphenyl, the entropic contributions to the free energy barriers are simple to estimate and are larger than some more complex contributions such as the MP4 correlation energy[15].

Overestimation of vibrational frequencies by HF methods is thoroughly documented, and the magnitudes of the computed frequencies for biphenyl are no exception[40]. Frequencies from a spectroscopically based force field[24] are an average of 10% less than their HF/3-21G counterparts. This systematic error is largely a consequence of neglecting electron correlation in the Hamiltonian, although basis set and anharmonic corrections can also be important.

Summarizing, perturbations to the vibrational spectrum of biphenyl with torsion do not change the zero-point energy, so that energetic and enthalpic barrier heights are the same. Changes to the vibrational partition function do influence the Gibbs free energy through a net decrease in vibrational disorder away from $\phi = 40°$.

Polymer properties

The molecular torsional potential has important implications for mechanical properties in the polymer. Effects that reduce ϕ, such as packing, cross-linking and mechanical pressure transverse to the chain axis, are expected to increase the stiffness. At first it seems surprising that forces which are formally orthogonal to the chain axis play a role in the stiffness. However, the torsional and tensile modes are coupled through the electronic structure of the biphenyl fragment.

Physically, the improved conjugation of the rings in a planar geometry enhances the quinoid form and strengthens the network of C–C bonds. Torsion and uniaxial stiffness are coupled through the molecular electronic structure. This quantum-mechanical coupling would be difficult to include in classical, empirical force fields that are used for molecular mechanics simulations.

In compression the isolated chains become more susceptible to bending as they get longer. In real polymers this bending is constrained by intermolecular forces and cross-linking. Therefore one would need to model the interactions between chains to describe and improve the compressive stiffness of PPP and other rigid-rod polymers. The bowed degrees of freedom corrupt even the Young's modulus, which is defined only at equilibrium, by adding soft, acoustic modes to the Hessian as the unit cell size increases.

Qualitative comparison of the stiffness calculated for biphenyl and a cluster model of PPP is useful, but a quantitative comparison is more difficult. Both pictures ignore intermolecular forces. Periodic boundary conditions in the cluster calculations provide additional resonance stabilization of the planar conformation, as well as doubling the ratio of inter- to intra-ring C–C bonds. The use of single determinant wave-functions is known to overestimate vibrational frequencies and, through the Hessian, the molecular stiffness. Using the biased Hessian approach of Dasgupta and Goddard[41] we have shown[4] that electron correlation reduces the AM1 modulus of polyethylene by 15%. Despite these quantitative drawbacks, we feel that analysis of polymeric fragments using *ab initio* and semiempirical molecular orbital methods permits a useful resolution of intra- and intermolecular contributions to the mechanical properties of polymers. In addition, the calculations

identify mechanisms for the interplay between mechanical strength and electronic structure which empirical force fields are less likely to resolve.

CONCLUSIONS

Chains of phenyl rings joined at the *para* position are very stiff in tension. Rotation of the rings about the chain axis is constrained by a torsional barrier whose height at 90° is half that at the planar conformation. Here we have extended previous calculations of the biphenyl torsion to include zero-point effects, which contribute equally to each stationary point on the HF surface, and entropic contributions, which differ in the D_2, D_{2d} and D_{2h} geometries.

The mechanical response of biphenyl shows a coupling between the torsional degree of freedom and uniaxial stress which, through intermolecular forces, is expected to influence the Young's modulus of bulk PPP. Alignment of the p-orbitals in the planar conformation stiffens the molecule by about 14%, a result which should also be true of a real polymer forced into a planar conformation by cross-linking, morphology or packing forces.

Variation of the compressive stiffness with the number of C_6H_4 rings in the unit cell has been ascribed to bending of the rigid rod. Buckling or bowing of the chain, which is constrained in a real polymer by intermolecular forces, also reduces the calculated modulus of an isolated chain by mixing softer vibrational modes into the equilibrium conformation.

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