Inter-ring Rotational Potential of Biphenyl and its Effect on Poly(p-phenylene)

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Detailed ab initio studies have been done on the inter-ring torsional states of the biphenyl molecule using self-consistent field molecular orbital method. The potential goes through a minimum at an angle of 38°. The height of the potential barrier for the coplanar state is 2.01 kcal/mol. When the phenyl rings are perpendicular to each other, this height increases to 2.37 kcal/mol. The role of correlation and polarization is found to be important. The shape of the potential suggests that poly(paraphenylene) may possibly exist as a super helix.

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Introduction

Poly(p-phenylene) [1] is one of the organic conjugated polymers that has caught the attention of experimentalists [2] and theoreticians [3] alike due to its \textit{dc} conductivity and other related properties which can have interesting potential applications. Normally \textit{\pi}-conjugated compounds are expected to be planar so that maximum overlap can occur between the \textit{\pi}-orbitals. However, in the case of polymers, steric hindrance can give rise to non-planarity in the chain. For a complete understanding of the mechanisms for conduction through the production of solitons or bipolarons, one needs to be assured of the geometries and the corresponding energetics of the polymers. In the case of poly para-phenylene (PPP), the non-planarity between two successive phenyl rings has been studied to a great extent using many different methods. These methods include semi-classical procedures [4–6], quantum mechanical semi-empirical methods [7–9], ab initio work [10–11], and molecular mechanics calculations [12]. However, in most cases there seems to be a great deal of discrepancy among these results.

In the present work, we have performed accurate ab initio calculations on the structure of biphenyl which consists of two links in the chain of PPP. The results aim to resolve the issue of the “correct” torsional angle and interlink bond length and thus provide a handle for an ab initio study of PPP. Choice
of proper wave functions and inclusion of correlation effects seem to play significant roles.

Method

Experimental evidence [13] seems to suggest that in a chain of PPP every alternate phenyl ring lies in the same plane. The unit that gets repeated is actually a biphenyl molecule with proper bonding between units to form a chain. In the present calculation, the biphenyl molecule was treated with no dangling bonds for simplicity in computation. The calculations were performed using a self-consistent-field (SCF) molecular orbital (MO) method where the atomic orbitals were represented by combinations of gaussians. This helped in analytical evaluation of the coulomb and exchange integrals leading to better accuracy in the computations.

For geometry optimization the energy of the molecule was calculated in a given conformation. Then the forces at chosen atomic sites were calculated and the atoms were relaxed till the forces became zero. In the present case (see Fig. 1) after choosing a basis set, all the C–C and C–H bonds in the rings were optimized with the phenyl rings maintained in the planar configuration. Then the rings were rotated about the C1–C1' bond. At each torsional angle \(\phi\), the value of \(R(C_1-C_1' \text{ bond length})\) was reoptimized and the total energy was obtained. A complete rotational potential energy curve was thus obtained between \(\phi = 0^\circ\) and \(\phi = 90^\circ\) for the chosen basis set.

It has been noticed [14] that proper representation of the atomic orbitals is necessary to obtain the correct interactions in a polymer chain. In particular, if an input basis set is too restrictive, one can obtain wrong potential energy curves. Therefore, we used the well-tested 4-31G split-valence basis set [15] in our calculations. Some previous calculations [16] have shown that in the case of conjugated polymers one could get the correct shape for the potential curve only by adding extra \(p\)-functions to the orbitals of hydrogens on the backbone. In order to cut down the computation time, we also followed this recipe and used a minimal STO-3G [17] basis set with the \(p\)-functions added to the hydrogens connected with the carbon atoms \(C_2, C_5, C_2', \text{ and } C_6\). This introduced enough flexibility in the STO-3G basis set to make it less restrictive so that the interactions were represented better. The results from both these basis sets are given in Fig. 2.

Correlation effects were introduced through second order perturbation [18]. In this case we used the STO-6G* basis set where the atomic orbitals were represented by six gaussians. This basis set also had extra \(d\)-functions for proper inclusion of polarization effects. The calculation was performed at SCF-MO level as well as with correlation. These results are also shown in Fig. 2.

Results and Discussion

To compare our results with those from various other calculations, we have presented all the results in Table 1. A quick glance shows that our optimized values for the \(C_1-C_1'\) bond length \(R\) for the planar configuration are, in general, slightly higher than the other results. However, it is quite comparable with the results of an ab initio work of Almlöf [10] which has used good double zeta quality atomic wave functions. The results from semiclassical [5, 6] and semi-empirical [7, 9] calculations are consistently shorter by a factor of approximately 10%. Similar behavior is also noticed from the molecular mechanics calculations [12]. The optimum values for \(R\) at \(\phi = 90^\circ\) are observed to be slightly less than that at \(\phi = 0^\circ\) except in the semi-classical and molecular mechanics calculations where the values for \(R\) remained constant.