Regular article

Molecular and electronic structures of bipolaron in poly-para-phenylene in terms of molecular orbital symmetry*

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Abstract. The molecular structures of the model systems of the polaron and the bipolaron in poly-para-phenylene (PPP) were calculated by an ab initio molecular orbital (MO) method with fairly sophisticated approximations. The calculated models are monocations, dications, monoanions and dianions of biphenyl, para-terphenyl, para-quaterphenyl, para-quinquephenyl and para-hexaphenyl. The calculations show that the longer the PPP oligomer is, the stronger is the tendency to take on a non-planar twisting structure. This was accounted for by the combination of repulsions between proximate ortho-hydrogen atoms with resonance interactions between benzene π MOs. The magnitude of the resonance interactions was assessed by using the symmetry of benzene π MOs as well as an analytical Hückel solution of the π MO for polyene. In addition, negatively charged polarons and bipolarons were found to have a stronger tendency to take on a planar structure than positively charged ones. This result was also explained by comparing the benzene π HOMO with the benzene π LUMO.

**Key words:** Poly-para-phenylene – Polaron – Molecular orbital symmetry

1 Introduction

Recently, many efforts have been made to obtain organic polymers with high electrical conductivity [1]. This is because conductive polymers are expected to have both the electrical conductivity of metals and the durability and light weight of plastics. Conductive polymers have often been referred to as synthetic metals.

In 1964, Little first proposed the possibility of high temperature superconductive polymers [2]. Then, the tetrathiafulvalene-tetracyanoquinodimethane complex (TTF-TCNQ) was found to have metallic conductivity. In 1975, the first superconductive polymer, polythiazyl, was found [3–5]. In 1977, polyacetylene was shown to have the high conductivity when doped [6, 7]. Since then, many kinds of highly conductive polymers have been synthesized and studied [8–14].

Except for polythiazyl, almost all the π conjugated polymer systems, such as poly-para-phenylene (PPP), show high electrical conductivity only when doped with electron donating or electron accepting agents. After doping, polymers develop solitons in polyacetylene or polarons/bipolarons in PPP. The molecular structures for these lattice defects should be intimately related to the mechanism of the electron conduction. In PPP two types of chemical structures may be considered, aromatic and quinoid:
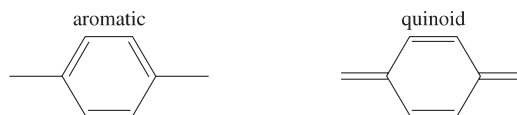
Since the total energy of a segment with aromatic structure is about 0.4 eV lower than that with quinoid structure, undoped polymers have the aromatic structure. When the polymers are doped, they become positively or negatively charged, leading to the formation of the quinoid form in order to stabilize the ionized system. The bipolaron found in PPP is a kind of localized excitation generated by adding two electrons to the system or by removing two electrons from the system. The formation of the bipolaron in PPP has been theoretically predicted [15–20] and also experimentally confirmed [21, 22]. In the bipolaron model, two centers with a net charge are coupled to each other in a restricted region, and consequently act as charge carriers. Since this situation is similar to that of the Cooper pairs in superconductors, it has been postulated that bipolarons will also support superconductivity [23]. Localized excitations such as charged solitons, polarons and bipolarons, which form in the polymer backbone upon oxidation or reduction, become charge carriers leading to the appearance of the conductivity in the polymer.

To study the relationship between the electrical conductivity of polymers and their molecular structural changes and electronic structural changes upon doping, ab initio molecular orbital (MO) methods extensively have been applied. The molecular structures and the vibrational frequencies of biphenyl (BP) and para-terphenyl (TP), which are oligomers of PPP, were calculated by ab initio SCF methods [24–26]. The electronic structure of quaterphenyl interacting with two Li atoms was calculated by ab initio SCF with minimal basis sets in order to investigate the relaxation of the molecular structure caused by the generation of charges in quaterphenyl [27]. The geometries of PPP oligomers with up to 11 phenyl groups were optimized for the neutral and dicationic species [28].

Previously we have been able to successfully predict the geometries of biphenyl in its ground and excited states in terms of orbital symmetries [29]. In the present article, we calculate the molecular structures of a series of PPP oligomers, BP, TP, para-quaterphenyl (QP), para-quinquephenyl (QQP) and para-hexaphenyl (HP), for the neutral, monocationic, dicationic, monoanionic, and dianionic species by ab initio MO calculations. From these calculations, it has been found that the longer the PPP oligomer is, the more the structure of the oligomer deviates from planarity. Furthermore, the tendency to take on the planar structure has been found to be in the following order:

dianion > dication > monoanion > monocation

> neutral form

These results are explained by using MO symmetry arguments as well as simple analytical solutions for the orbital energies of polyene by the Hückel method.

2 Method

Ab initio MO calculations were performed using an STO-3G basis set of the Gaussian92 program package [30] throughout this study unless otherwise noted. Such a minimal basis is adequate for a qualitative description of the relationship between molecular structure and orbital symmetry. We have used Gaussian92 to calculate the total energy and the electronic structure and to obtain the optimized geometry for the PPP oligomers.

3 Results and discussion

Table 1 shows the optimized dihedral angles in the PPP oligomers. As can be seen, the neutral oligomers are twisted while the charged species are more planar. This tendency is remarkable for the relatively short PPP oligomers BP and TP. The longer PPP oligomers, have a mixture of planar and twisted sections. This is in agreement with the assumption that polarons and bipolarons are limited to a finite length. Note also that the tendency to a planar structure is stronger for dications and dianions (the model for a bipolaron) than for monocations and monoanions (polaron model). Moreover, dianions are more planar than dications, and monoanions more planar than monocations. To make sure that these results are not an artifact of the calculational method, we repeated the process with HF/3-21G and MP-2/3-21G basis sets (Table 2). It is obvious that the calculated tendency toward planarity does not depend on the approximation used, although the absolute magnitude of the torsional angles are slightly different.

It is these characteristics of the polaron and the bipolaron geometry that are primarily connected with the physico-chemical properties of PPP, such as electronic conductivity. In this paper we will try to explain their significance on the basis of the MO symmetries. We first examine the case of BP. In 1968, the geometry of BP in the excited state was elegantly presented by Imamura and Hoffmann [29] in terms of the symmetry of benzene MOs. In that work, the π MOs of planar BP were constructed from the π MOs of two benzenes in the same plane, and for perpendicularly twisted BP the π MOs of two non-interacting benzene rings were used. The energy diagram for this system is depicted in Fig. 1. From this data, it is obvious that the total π electronic energy is, to a first approximation, the same in both the perpendicular and planar forms of ground state BP. This is because the destabilization energy of the SA MO is

Table 1. Dihedral angles [deg] between neighboring benzene rings in PPP oligomers; fully optimized ab initio MO with STO-3G basis set. The angle notation is given below the table

	Angle	Neutral	Dianion	Dication	Monoanion	Monocation
Biphenyl	B1	39.6	0.0	0.0	0.0	2.3
Terphenyl	B1 (= B2)	39.1	0.0	0.0	5.3	17.9
Quaterphenyl	B1	38.8	0.1	0.0	0.9	7.0
	B2 (= B3)	39.0	0.1	0.0	22.5	28.1
Quinquephenyl	B1 (= B2)	39.0	0.0	0.2	2.7	14.4
	B3 (= B4)	38.7	0.1	15.1	30.7	34.2
Hexaphenyl	B1	38.7	0.0	0.1	1.1	8.1
	B2 (= B3)	38.6	0.2	0.3	20.2	25.3
	B4 (= B5)	39.0	18.4	25.3	34.9	36.9

Quaterphenyl

B2 B1 B3

Quinquephenyl

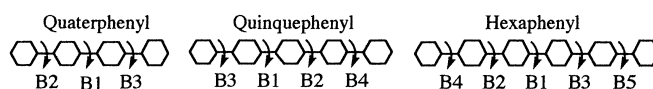B3 B1 B2 B4

Hexaphenyl

B4 B2 B1 B3 B5

Table 2. Dihedral angles [deg] (see Table 1) and carbon-carbon bond lengths (CC)[Å] between benzene rings in PPP oligomers calculated with three different basis sets

Basis set		HF/STO-3G	HF/3-21G	MP2/3-21G
Biphenyl				
neutral	B1	39.6	52.0	52.2
	CC	1.5080	1.4902	1.4938
dication	B1	0.0	0.1	0.1
	CC	1.3768	1.3662	1.4168
dianion	B1	0.0	0.0	0.0
	CC	1.3596	1.3668	1.4090
Terphenyl				
neutral	B1 (=B2)	39.1	51.5	
	CC	1.5071	1.4896	
dication	B1 (=B2)	0.0	0.0	
	CC	1.3996	1.3882	
dianion	B1 (=B2)	0.0	0.0	
	CC	1.3853	1.3892	

canceled out by the stabilization energy of the SS MO. However, the BP is still expected to take the twisted form to minimize repulsion between ortho-hydrogen atoms. Also there is no notable stabilization energy arising from possible π-conjugation in the planar configuration. On the other hand, in the lowest excited state in which both the SS LUMO and the SA HOMO have an electron, the above-mentioned cancellation can no longer occur, as shown in Fig. 1. Thus, for the excited state, the planar form is expected to be much more stable than the twisted form because the stabilization by π-conjugation overcomes the repulsion between ortho-hydrogen atoms. Therefore, the symmetry of the MOs plays an important role in the determination of the geometry of BP for the ground and the excited states.

We now turn to the charged PPP oligomers, that is, those containing polarons and bipolarons. In the following calculations, all parameters of the geometries of the positively or negatively charged molecules were fixed at those of the neutral except for the torsional angles between adjacent benzene rings. All calculations were carried out with an STO-3G basis set which is sufficient to reproduce the essential features of PPP and also to enable a study of longer PPP oligomers within a minimum of computation time.

In Table 3, the obtained torsional angles are listed for the monocations, monoanions, dications and dianions together with those of the neutrals. The absolute values for twisting angles are different from those in Table 1 for charged species. However, as before, we found that the longer the PPP oligomer is, the stronger the tendency to take on a twisting-configuration in charged species, but for neutral species the twisting angles do not depend on the length of oligomers. The tendency towards planarity follows the following dianions > dications > monoanions > monocations. Consequently, we can say that the tendency for the change of geometry is not dependent strongly on the bond lengths and the bond angles being fixed at those for the neutral species.

In order to connect the MO symmetry to the change in the total energy, we depict the π orbital energies of the neutral PPP oligomers in Fig. 2. In this figure, the energy levels which originate from the benzene HOMO
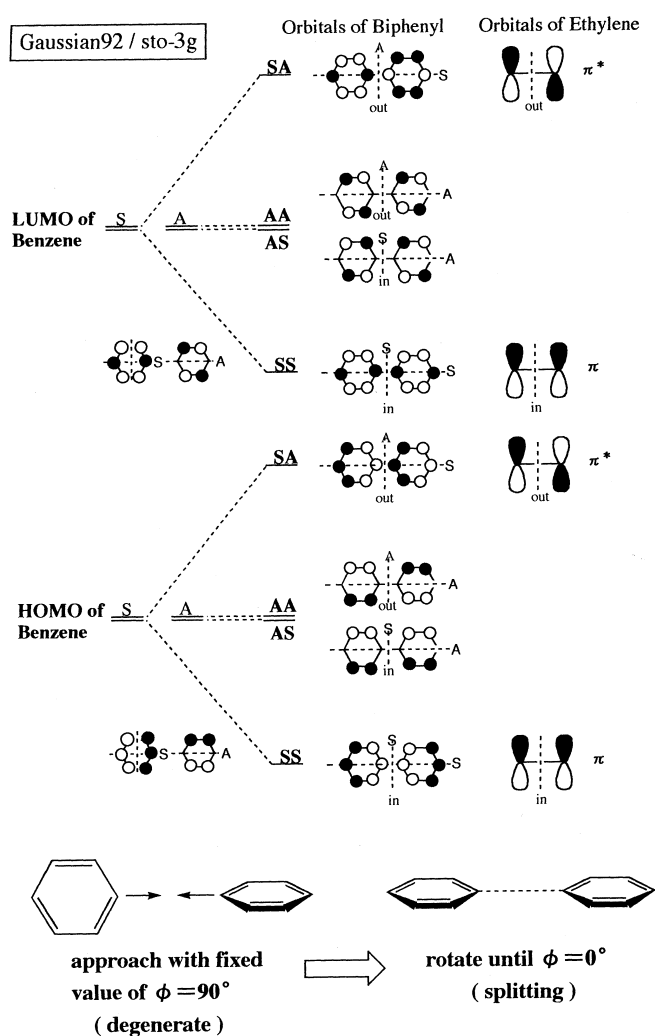

Fig. 1. Energy level diagram for molecular orbitals (MOs) of biphenyl calculated with an STO-3G basis set. The bottom part of the figure shows two benzene rings perpendicular to each other ($\phi = 90°$) and thus noninteracting. Their separate MOs are degenerate. When the dihedral angle ϕ is allowed to decrease to 0°, the benzene MOs begin to interact – splitting occurs. This is shown in the *upper part* of the figure: at left the separate degenerate HOMOs (4 each) and LUMOs (4 each) of the two benzene rings symmetric (S) and antisymmetric (A) with respect to a common axis of symmetry, then splitting into (4 each) biphenyl orbitals, now symmetric (S) or antisymmetric (A) with respect to two symmetry axes. At *right* are shown the orbitals of ethylene which correspond to the in phase and out of phase interactions of two benzene MO in biphenyl

with S symmetry are shown, and the ordinate represents the difference between the MO energy of the PPP oligomer and the energy of the benzene HOMO. It should be noted that the arrangement of the orbital energies for these molecules corresponds quite well to the energy levels for polyene, shown in Fig. 3, in which the orbital energy levels for BP correspond to those for ethylene, those for TP to those for allyl radical, those for QP to those for butadiene, and so on. This result should be expected given that the benzene HOMO with S symmetry in PPP corresponds to the $2p$ π atomic orbital in polyene.

Table 3. Values of optimized dihedral angles [deg] between neighboring benzene rings in PPP oligomers. All other parameters of the molecular geometry were fixed at the values for the neutral species. See Table 1 for the angle notation

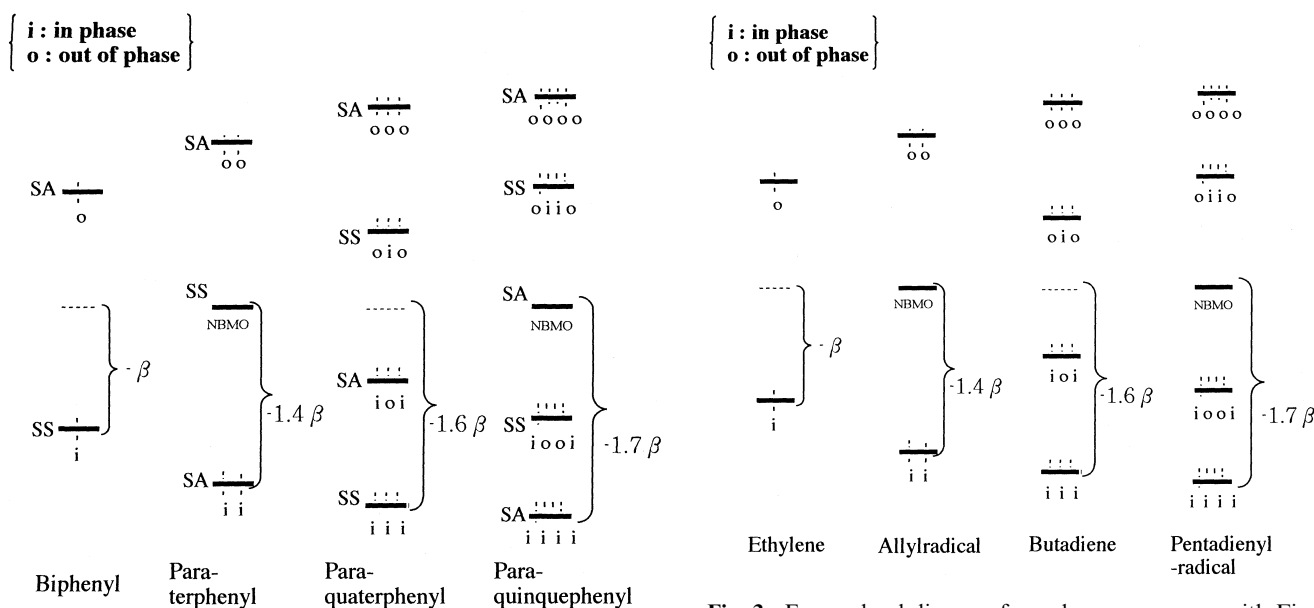| Oligomer	Angle	Neutral	Dianion	Dication	Monoanion	Monocation
Biphenyl	B1	39.6	0.0	0.0	10.1	15.8
Terphenyl	B1 (= B2)	39.1	0.1	0.0	19.1	22.5
Quaterphenyl	B1	38.8	0.5	0.1	13.8	16.2
	B2 (= B3)	39.0	1.2	0.1	26.9	29.2
Quinquephenyl	B1 (= B2)	39.0	1.8	8.0	18.5	20.7
	B3 (= B4)	38.7	18.1	20.9	32.4	34.1
Hexaphenyl	B1	38.7	2.9	7.6	15.4	17.3
	B2 (= B3)	38.6	11.5	13.4	25.1	27.1
	B4 (= B5)	39.0	22.8	24.7	35.5	36.6

Fig. 2. Energy level diagrams for PPP oligomers. The electron distribution corresponds to the ground state neutrals. β is the resonance integral between two neighboring benzene rings (Eq. 1) $\frac{\cdot\ \cdot}{\cdot}$, $\frac{\cdot\ \cdot}{\cdot\ \cdot}$ etc symbolize the nodal plane in MO

Fig. 3. Energy level diagram for polyenes, compare with Fig. 2

For a series of neutral PPP oligomers, in the first approximation, the geometry change from perpendicular to planar gives rise to no π electron stabilization energy. In BP and QP this is because all the stabilization energy due to π electrons in the SS MO are completely canceled out by π electrons in the SA MO. For TP and QQP stabilization by electrons in the lowest MO with SA symmetry is canceled out by electrons in the highest MO with SA symmetry, as is shown in Fig. 4. Thus, one sees no change in stabilization with increasing oligomer length. On the other hand, the repulsion energy between ortho-hydrogen atoms increases proportionally with the number of benzene rings (strictly speaking, the number of benzene rings less 1) as can be seen from Fig. 5. Because the total energy is the sum of the stabilization and repulsion energies, one sees an increased tendency to twist with increasing length and the twisted form is always more stable than the planar configuration. As can be seen from Fig. 6 it is thus the ortho-hydrogen re-

pulsion that is the determining factor in the structure of PPP oligomers, at least in the first approximation.

Next, we proceed to the analysis of the positively and the negatively charged PPP oligomers. For consistency with Fig. 2, we indicate in Fig. 7 the change in the orbital energies that occurs when two perpendicularly oriented benzenes interact to form a planar BP. The BP dication is more stable than two benzenes because of the empty BP SA orbital. The dianion of BP is also more stable than two perpendicularly arranged benzenes. Here it is because the two electrons of the LUMO of the benzenes are now in a bonding SS MO of BP.

The electron distributions in the MOs of the other PPP oligomers are shown in Fig. 8. The stabilization energy arising from the transition from a structure of perpendicularly arranged benzene rings to a planar PPP structure was approximated by using the Hückel orbital energy for polyene, that is

$$\varepsilon_i = \alpha + 2\beta\cos[i\pi/(n+1)]$$
$$i = 1, 2, 3, \ldots, n \tag{1}$$

where $n = 2$ corresponds to BP, $n = 3$ to TP, $n = 4$ to QP and so on, α is the energy of the benzene HOMO and β is the resonance integral between two neighboring
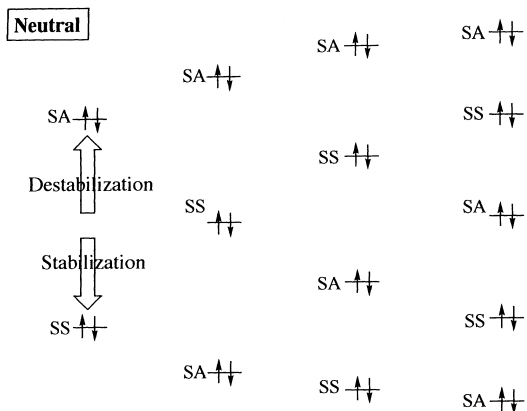
Fig. 4. Energy level diagram for a series of neutral PPP oligomers, derived from HOMO symmetrical orbitals of benzene

Fig. 7. Electron distribution in dication and dianion BP MOs derived from the HOMO and LUMO of two perpendicularly oriented benzene molecules
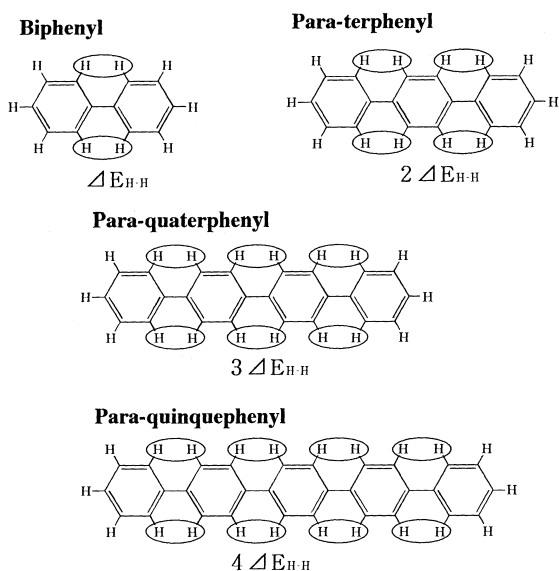

Fig. 5. Contribution of the repulsion energy between ortho-hydrogen atoms to the total energy as a function of the number of benzene rings. See Fig. 6
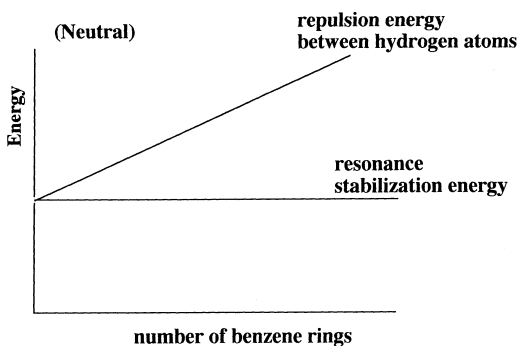

$$\varepsilon_i = \alpha + 2\beta \cos(i\pi/n+1) \qquad i=1,2,3,\cdots$$

Fig. 8. Schematic of the resonance stabilization energy for dications of PPP oligomers derived from the analytical Hückel solution for polyene

Fig. 6. The repulsion energy between ortho-hydrogen atoms and the resonance stabilization energy as a function of the number of benzene rings for neutral PPP oligomers
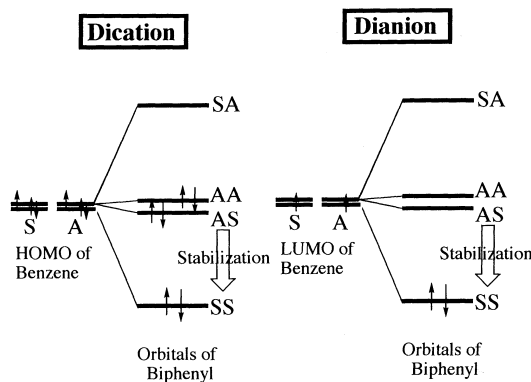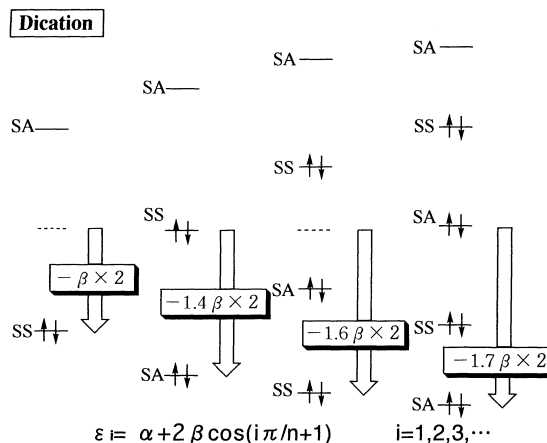
benzene HOMOs with S symmetry, since the benzene HOMO with S symmetry is equivalent to the $2p\,\pi$ atomic orbital in polyene. The resonance stabilization energy depends on the energy of the lowest MO in Fig. 8, that is,

$$\Delta E = 4(-\beta)\cos[\pi/(n+1)] \qquad (2)$$

It should be pointed out that the magnitude of ΔE found by Eq. 2 increases gradually with the number of benzene rings n, but the increment of ΔE decreases gradually as n increases, contrary to the linear increase in the repulsion energy between neighboring ortho-hydrogen atoms shown in Fig. 5. As before, the preference for the planar structure over the twisted structure should be controlled by the sum of the resonance stabilization energy and the repulsion energy between ortho-hydrogen atoms. Consequently, we can expect that the planar structure is more stable than the twisted structure for the shorter PPP oligomers while the reverse is true for the longer PPP oligomers, as is schematically depicted in Fig. 9.

Figure 9 also shows the data for the monocation. We expect similar behavior to the dication since the only difference is that there is now one electron in the upper
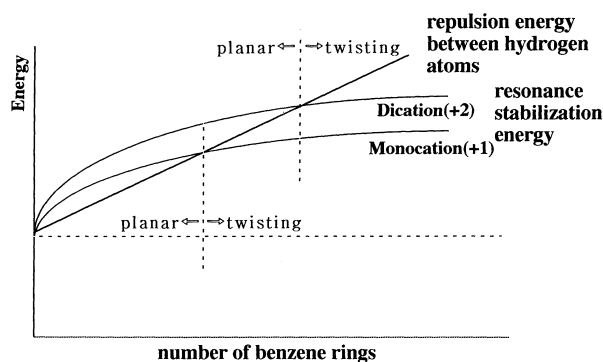
Fig. 9. Repulsion energy between ortho-hydrogen atoms and resonance stabilization energy for dications and monocations of PPP oligomers as a function of the number of benzene rings. When the stabilization energy is greater than the repulsion energy the oligomer tends to planarity, otherwise a twisted structure is preferred

SA orbitals shown in Fig. 8, leading to a lower, by half, stabilization ΔE. Therefore, the tend to twist at shorter chain lengths than the dications do.

A similar tendency is expected for the monoanions and dianions of the PPP oligomers. If we recall the picture in Fig. 7, the BP dianion is also more stable than two separate benzenes. A similar trend holds for the longer oligomers. Again, the stabilization energy for the monoanions would be simply less by half of ΔE for the corresponding dianions.

These predictions of the preferred conformations are consistent with the calculated molecular structures derived from the total energy as shown by the data in Table 2.

Note that the resonance stabilization energy ΔE is derived not from the total energy of the system, but from the energies of the MOs of the separated benzenes. To check whether orbital symmetry influences the total energy, we can treat the system analytically, excluding all symmetry arguments. We assume that the total energy can be represented for the neutral molecules and for the dications by Eq. (3) and Eq(4), respectively.

$$E(\text{neutral}) = E_0^{\text{N}} + \{\Delta E^{\text{H-H}} + 0 + \Delta E^{\text{RE2}}\} \qquad (3)$$

$$E(\text{dication}) = E_0^{\text{DC}} + \{\Delta E^{\text{H-H}} + \Delta E^{\text{RE1}} + \Delta E^{\text{RE2}}\} \qquad (4)$$

where E_0^{N} and E_0^{DC} denote the terms of the total energy which do not depend on the twisting angle between neighboring benzene rings, and $\Delta E^{\text{H-H}}$ represents the repulsion energy between ortho-hydrogen atoms. ΔE^{RE1} is the resonance stabilization energy from the interaction between HOMOs or LUMOs of the isolated benzene π orbitals, that is, ΔE^{RE1} is equivalent to the first order perturbation energy. (In the neutral molecules, ΔE^{RE1} should be negligibly small because of the mutual cancellation of the stabilization and the destabilization and is therefore omitted in Eq. (3)) ΔE^{RE2} is the delocalization energy of π electrons from occupied orbitals of a benzene ring to unoccupied orbitals of a neighboring benzene ring, that is, ΔE^{RE2} corresponds to the second order perturbation energy. $\Delta E^{\text{H-H}}$, ΔE^{RE1} and ΔE^{RE2} are all dependent on the torsional angle between

neighboring benzene rings. Taking the difference of Eqs. (3) and (4) we obtain

$$E(\text{neutral}) - E(\text{dication}) = (E_0^{\text{N}} - E_0^{\text{DC}}) - \Delta E^{\text{RE1}} \qquad (5)$$

Strictly speaking, ΔE^{RE2} for neutral molecules may be slightly different from ΔE^{RE2} for dications. However, we have, in the first approximation, neglected this in Eq. (5).

When the sum of the orbital energies of a molecule is proportional to the total energy, ΔE^{RE1} can be represented

$$\Delta E^{\text{RE1}} = \alpha + 2\beta \cos[\pi/(n+1)] \qquad (6)$$

and

$$\begin{aligned}
\Delta E &= E(\text{neutral}) - E(\text{dication}) \\
&= (E_0^{\text{N}} - E_0^{\text{DC}}) - \alpha - 2\beta \cos[\pi/(n+1)] \qquad (7) \\
&= \alpha' - 2\beta \cos[\pi/(n+1)]
\end{aligned}$$

where n is the number of benzene rings. We can find α' and β by solving the equation for some known E_0^{N} and E_0^{DC}; we have done this for $n = 2$ (BP) and $n = 3$ (TP). Then, by substituting the derived α' and β (Fig. 10), we can find the ΔE for larger oligomers. To double check the results, the derived ΔE's were plugged into

$$\Delta E = \alpha' - 2\beta x \qquad (8)$$

and the obtained x values were compared to $\cos[\pi/(n+1)]$. Both the analytically derived ΔE values, using α' and β found from $n = 2$ and $n = 3$ and the MO derived values are listed in Table 4. The agreement is quite remarkable. Thus, it can be concluded that the two factors of the resonance stabilization energy ΔE^{RE1} and the repulsion energy between the ortho-hydrogen atoms control the geometry (planar or twisted) of the PPP oligomers. A similar analysis was carried out for the dianions, monocations and monoanions. The results are depicted in Fig. 11. Obviously, the magnitudes of the resonance stabilization energy follow the ordering

dianion > dication ≫ monoanion > monocation

and this ordering is completely consistent with the results on the molecular structures obtained by both the partial optimization of torsional angles (Table 3) and the full geometry optimization (Table 1 or 2).

Finally, we would like to know why the dianionic species has a stronger tendency toward a planar structure than the dicationic species and similarly, the monoanionic and monocationic species. We compared the MOs of the BP dianion to those of the BP dication. A large difference in the magnitude of the coefficients on the carbon atoms which combine two phenyl rings was found. In Fig. 12, the coefficients of carbon $2p$ π orbitals are shown for the benzene HOMO with SA symmetry and the LUMO with SS symmetry. From these, we can evaluate approximately the relative magnitude of the orbital energy changes due to the interaction between two identical benzene HOMOs or LUMOs via the following equation [31]:

$$\Delta E \sim (\varepsilon_i + F_{ii'})/(1 + S_{ii'}) - \varepsilon_i = (F_{ii'} - S_{ii'}\varepsilon_i)/(1 + S_{ii'}) \qquad (9)$$

(Analytical solution)

$$\varepsilon_i = \alpha + 2\beta \cos(i\pi/n+1)$$
$$i = 1,2,3,\cdots$$

Gaussian92/sto-3g

$$E(neutral) - E(dication) = (E_0^N - E_0^{DC}) - \Delta E^{RE1}$$
$$E(neutral) - E(dianion) = (E_0^N - E_0^{DA}) - \Delta E^{RE1}$$
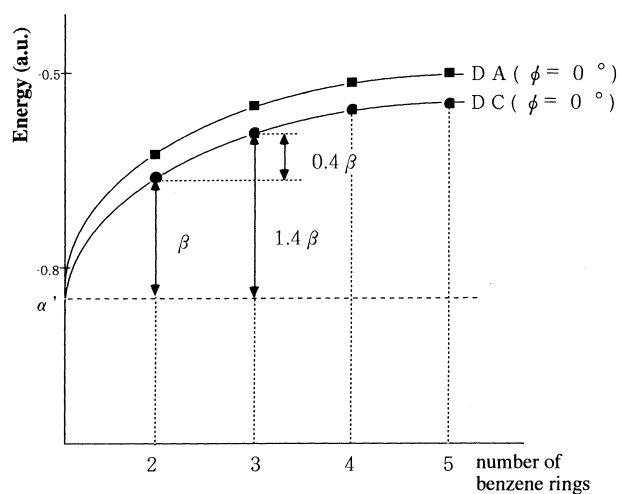
Fig. 10. E (neutral) $- E$ (dication) and E (neutral) $- E$ (dianion) as a function of the number of benzene rings. α' and β are parameters of the Hückel analytical solutions, Eqs. 6–8. DA denotes dianion, DC dication, and ϕ is the dihedral angle between neighboring benzene rings
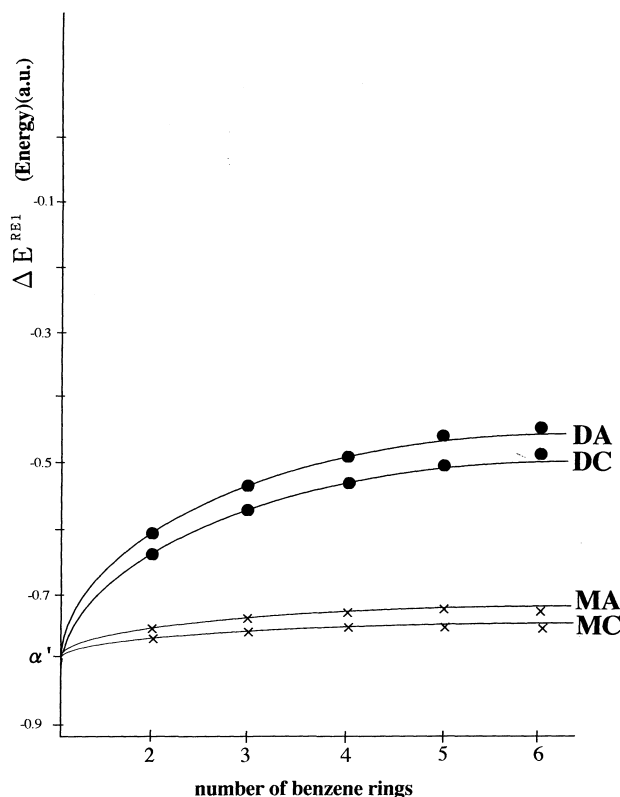

Fig. 11. Resonance stabilization energies (first order perturbation) in going from neutral to charged species, as a function of the number of benezene rings, calculated by ab initio MO calculations (● and x) and by Eq. (7) (*lines*). MA denotes monoanion, MC monocation, DA dianion, DC dication. In this figure, α' for MA, MC, DA and DC is taken as a standard

Table 4. Comparison of the Hückel analytical solution for the stabilization energy of PPP oligomers with values calculated by an MO method with a fitting parameter β

Number of rings	2	3	4	5	6
Analytical solution (Eg. 7)	β	$1.41421\,\beta$	$1.61803\,\beta$	$1.73205\,\beta$	$1.80194\,\beta$
Calculated value (Eg. 8) ($\phi = 0.0°$)					
Dication	β	$1.41421\,\beta$	$1.63354\,\beta$	$1.76585\,\beta$	$1.85464\,\beta$
Dianion	β	$1.41421\,\beta$	$1.63147\,\beta$	$1.76247\,\beta$	$1.84936\,\beta$

$F_{ii'}$ and $S_{ii'}$ are the Fock and the overlap integrals between the i-th and i'-th orbitals, and ε_i is the corresponding i-th orbital energy. i and i' denote the HOMOs of two benzenes or the LUMOs of two benzenes. From this equation, ΔE for the LUMO is expected to be larger than ΔE for the HOMO since the orbital energy ε_i is positive for the LUMO and negative for the HOMO. This makes the second term of the numerator in Eq. (9) larger for the LUMO, yielding a larger ΔE: -0.05050 a.u. vs. -0.04155 a.u. for the HOMO. In other words, a dianion obtains more stabilization energy by taking on the planar structure than its corresponding dication. The same is true for the relative magnitudes of the stabilization energies of monoanions and monocations. This discussion supports completely the results obtained from ab initio MO calculations.

4 Conclusions

The molecular structures of polarons and bipolarons in PPP oligomers have been found to depend upon the resonance interaction between benzene π orbitals and the repulsion between ortho-hydrogen atoms on neighboring benzenes. The magnitude of the repulsion energy between ortho-hydrogen atoms is linearly dependent on the length of the PPP oligomers, as is expected from the number of pairs of proximate ortho-hydrogen atoms. The magnitude of the resonance interactions between benzene π orbitals in polarons and bipolarons of PPP oligomers can be approximated by the analytical Hückel solution of the lowest π orbital energy for polyene. It was found that the longer the PPP oligomer, the more gradually the magnitude of the resonance interactions increases. This was explained by taking the symmetry of benzene MOs into account. The net result of the
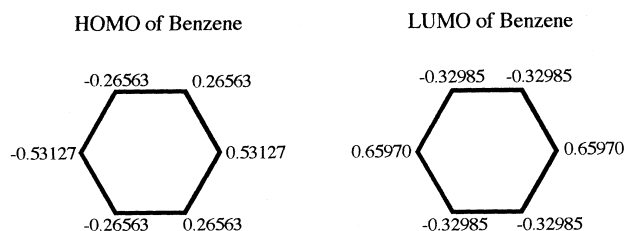
Fig. 12. Carbon atom orbital coefficients of the benzene HOMO and LUMO

repulsion energy and resonance interactions is that the polarons and the bipolarons in short PPP oligomers have a strong tendency toward a planar structure while longer PPP oligomers tend toward non-planar, twisting structures. This is in complete agreement with ab initio MO calculations, supporting the analysis used here.

Negatively charged polarons and bipolarons are more likely to be planer than positively charged ones. This trend was explained by the magnitude of the atomic orbital coefficients of the HOMO and LUMO of benzene.

In conclusion we can say that the molecular structure of polarons and bipolarons in PPP can be reasonably inferred from the symmetry of benzene MOs as well as the repulsions between ortho-hydrogen atoms. This method for analysis can be applied to other systems such as poly-para-phenylenevinylene, polypyrrole and so on, and is currently in progress.

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