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## Molecular Simulation

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### Modelling of Structural and Vibrational Properties of Poly(*p*-Phenylene) and Polypyrrole Using Molecular Orbital Methods

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# MODELLING OF STRUCTURAL AND VIBRATIONAL PROPERTIES OF POLY(*p*-PHENYLENE) AND POLYPYRROLE USING MOLECULAR ORBITAL METHODS

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This paper concentrates on two very important conducting polymers poly(*p*-phenylene) and polypyrrole. Detailed atomistic molecular models have been developed with the help of *ab initio* and semi-empirical quantum mechanical calculations using the Cerius<sup>2</sup> and WinMOPAC (version 6.0) programs.

Their optimised geometry had been calculated and compared with experimental X-ray diffraction data. The simulated and experimental vibrational spectra of biphenyl as well as isolated pyrrole monomers and oligomers from  $n = 1$  and 2, where  $n$  is the number of structural repeat units used, have been computed using the *ab initio* 3–21G basis set. The results obtained are compared with experimental data for the case of biphenyl and for oligomers with  $n = 2$  to 5 for both neutral benzenoid and quinonoid oligopyrroles, from semi-empirical predictions obtained by AM1 and PM3. The trends in the computed harmonic force fields, vibrational frequencies and intensities are monitored as a function of the chain length. The data are analyzed in conjunction with the trends in computed equilibrium geometries.

**Keywords:** Poly(*p*-phenylene); polypyrrole; MO methods

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## INTRODUCTION

Electronically conducting polymers are an extremely promising category of materials. In practice, most electronically conductive polymers are not easily processable in their pure form. Although high-capacity polypyrrole capacitors [1] and rechargeable polyaniline batteries [2] are in commercial production, it is generally thought that the potential of conducting polymers has not nearly been tapped. Vibrational spectroscopy is one of the most important and promising tools for the characterization of organic, polyconjugated polymers in the undoped, as well as in the doped state [3]. However, particularly in the doped case, detailed information on the microstructure of the materials in terms of bond lengths and bond angles is not easily derived because of the substantial amount of disorder present. In the doped state, localized charged defects are formed on the polymer chains [4]. These arise because of the interaction with the dopant and the subsequent electron transfer from or to the dopant. The nature of the defects their structure including that of the counterion position, and their role in the conduction process, is still not well understood. Positive and negative polarons as well as bipolarons have been suggested as charge carriers [4].

Among the various aromatic polyconjugated polymers, polypyrrole is one of the most thoroughly investigated systems [3]. Polypyrrole or poly(*p*-phenylene), as opposed to polyacetylene and polythiopyrrole, belongs to the class of electrically conducting polymers with a nondegenerate ground state, *e.g.*, the energy of the ring and other derived properties depend on whether the five- or six-membered rings have a benzenoid or a quinonoid C—C bond length alternation pattern.

Historically, there have been difficulties in obtaining structurally well defined polymer samples and this led to numerous attempts to synthesize short oligopyrroles with defined chain length [5]. The vibrational spectra of these oligopyrroles were studied experimentally in the neutral state. So far, a few theoretical investigations [3] have been carried out on the structures and spectroscopic characteristics of the oligomers. There is some discussion in the literature regarding the molecular orbital method best suited to calculating electronic structures, *e.g.*, Cornil, Beljonne and Bredas [6] use AM1 (Austin Model 1) geometries coupled with INDO/CI (Intermediate Neglect of Differential Overlap/Configuration Interaction) which reproduces the localisation of charge carriers better than the corresponding UHF (Unrestricted Hartree-Fock) method they note that the INDO/CI approach allows the analysis of the linear and nonlinear optical response, as this is the

property of most interest to them. This study is primarily focused on the vibrational spectra and not the electronic properties, so a semi-empirical method has been chosen to reproduce the geometries.

## EXPERIMENTAL/INITIAL STATES

### Modelling the *p*-phenylene Monomer

The modelling work presented here was performed on three platforms. The work on modelling all of the phenylene compounds was performed on a Silicon Graphics IndigoRS4600 and two RS4000 machines. The software used on these was Cerius<sup>2</sup>; Gaussian94 [7] and Insight [7]. Before commencing the modelling of the poly(*p*-phenylene), the modelling of the single monomer units was performed. The determination of an ideal model of each of the constituent parts of the polymers was modelled. In this brief study, experimental data, (taken from biphenyl models for Lignin investigated by X-ray Crystallography and NMR spectroscopy [8] and deposited in the Cambridge Crystallographic Database [9]), for the constituent monomer were used, as this seemed to be the ideal data, from which to start the modelling. The minimised structure using MOPAC and the structure minimised with partial charges, were analysed in terms of their energy and geometric values.

### Modelling the Bipyrrrole ( $n = 2$ )

In the case of the *ab initio* calculations on the 2PPy, on the series of benzenoid oligopyrroles, *n*PPy ( $n = 1 - 2$ ), and on the corresponding quinonoid oligopyrroles, *Qn*PPy, with  $n = 1$  to 2, we used the 3-21 G\* basis set.

### Molecular Orbital Modelling of Poly(*p*-phenylene)

The repeat unit of the poly(*p*-phenylene) (two sub-units) to be used in the simulation was built using the molecular orbital model in the experimental section. The repeat unit in this case was designed to have one head and one tail so that the model would link up into a linear thermoplastic polymer. Random structures were generated by the amorphous builder at a default temperature of 273.15 K.

The unit cell parameters and space group information for (*p*-phenylene) are shown below:

**Fixed Coordinate System: Cartesian**

Cell parameters:  $a = 4.52 \text{ \AA}$ ,  $b = 9.1 \text{ \AA}$ ,  $c = 2.8 \text{ \AA}$

Cell angles:  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ .

**Space Group Information**

Full name: P1

Lattice type: Monoclinic A

Lattice centering: Primitive

Lattice points at (0, 0, 0)

Poly(*p*-phenylene) (comprising two and three sub-units) was modelled using MOPAC [7], included in the Cerius<sup>2</sup> [7] environment, the polymer modelling package from Molecular Simulations Inc. [7] The method used was AM1, one of the default methods present in the modelling package. An initial model was built with the 3-D sketcher from crystal data taken from the Cambridge Crystallographic Database [9]. Geometry optimisation and frequency calculations using MOPAC were performed on the system using atoms with partial atomic charges calculated from MOPAC on the system. The geometry of the resulting systems was measured. This consisted of the relevant bond lengths, bond angles and torsional angles of the system and a comparison with experimental results is given in Tables I, II and Figure 1.

Previous work has indicated the close correlation between the bond lengths produced by the AM1 method, *ab-initio* molecular orbital calculations using the 3–21 G basis set and experimental results for phenyl rings [10] and our results also agree with this conclusion.

In two experimental cases [11, 12], the dimer has characteristic inter-ring bond distances of  $2.0 \sim 3.2 \text{ \AA}$  which are very similar to the simulated inter-ring bond distance of  $2.6 \text{ \AA}$ .

**Molecular Orbital Modelling of Polypyrrole**

Polypyrrole (two to five structural repeat units) was modelled using MOPAC [7], included in the Cerius<sup>2</sup> [7] environment, the polymer modelling package from Molecular Simulations Inc. The methods [7] used were AM1 and PM3, two of the default methods present in the modelling package as AM1 and MNDO.

The geometry of the resulting systems was measured and compared and comes on agreement with previous studies [13]. This consisted of the relevant bond lengths, bond angles and torsional angles of the system, Tables III–V.

TABLE I Table comparing experimental and simulated bond lengths of the atoms in the biphenylene

<i>Atom</i>	<i>Experimental bond length/<math>\text{\AA}</math></i>	<i>Simulated bond length/<math>\text{\AA}</math></i>	<i>Atom</i>	<i>Atom</i>	<i>Atom</i>
C7			C7		
C13	1.46	1.46	C13	C7	
C15	1.40	1.40	C15	C13	C7
C17	1.38	1.39	C17	C15	C13
C19	1.38	1.39	C19	C17	C15
C21	1.38	1.39	C13	C7	C15
C23	1.40	1.40	C23	C13	C21
H24	1.10	1.11	C21	C19	C23
H22	1.10	1.10	C19	C17	C21
H20	1.10	1.10	C17	C15	C19
H18	1.10	1.09	C15	C13	C17
H16	1.10	1.10	C7	C13	C15
C5	1.40	1.40	C5	C7	C13
C3	1.38	1.39	C3	C5	C7
C1	1.38	1.39	C1	C3	C5
C11	1.38	1.39	C7	C13	C5
C9	1.40	1.40	C9	C13	C5
H10	1.10	1.10	C11	C1	C9
H12	1.10	1.10	C1	C3	C11
H2	1.10	1.09	C3	C5	C1
H4	1.10	1.10	C5	C7	C3
H6	1.10	1.10			

TABLE II Table comparing experimental and simulated torsional angles of the atoms in the biphenylene

<i>Atom</i>	<i>Experimental torsional angle/<math>^{\circ}</math></i>	<i>Simulated torsional angle/<math>^{\circ}</math></i>	<i>Atom</i>	<i>Atom</i>	<i>Atom</i>
C7			C7		
C13			C13	C7	
C15			C15	C13	C7
C17	-179.9	-179.9	C17	C15	C13
C19	0.3	0.2	C19	C17	C15
C21	0.0	0.0	C13	C7	C15
C23	-179.4	-179.5	C23	C13	C21
H24	-179.7	-179.7	C21	C19	C23
H22	179.9	179.8	C19	C17	C21
H20	179.9	179.9	C17	C15	C19
H18	-179.8	-179.9	C15	C13	C17
H16	-179.3	-179.4	C7	C13	C15
C5	40.0	40.1	C5	C7	C13
C3	179.5	179.5	C3	C5	C7
C1	0.0	0.0	C1	C3	C5
C11	0.0	0.1	C7	C13	C5
C9	179.5	179.5	C9	C13	C5
H10	-179.5	-179.5	C11	C1	C9
H12	179.3	179.4	C1	C3	C11
H2	180.0	180.0	C3	C5	C1
H4	-179.8	-179.8	C5	C7	C3
H6	-179.8	-179.7			

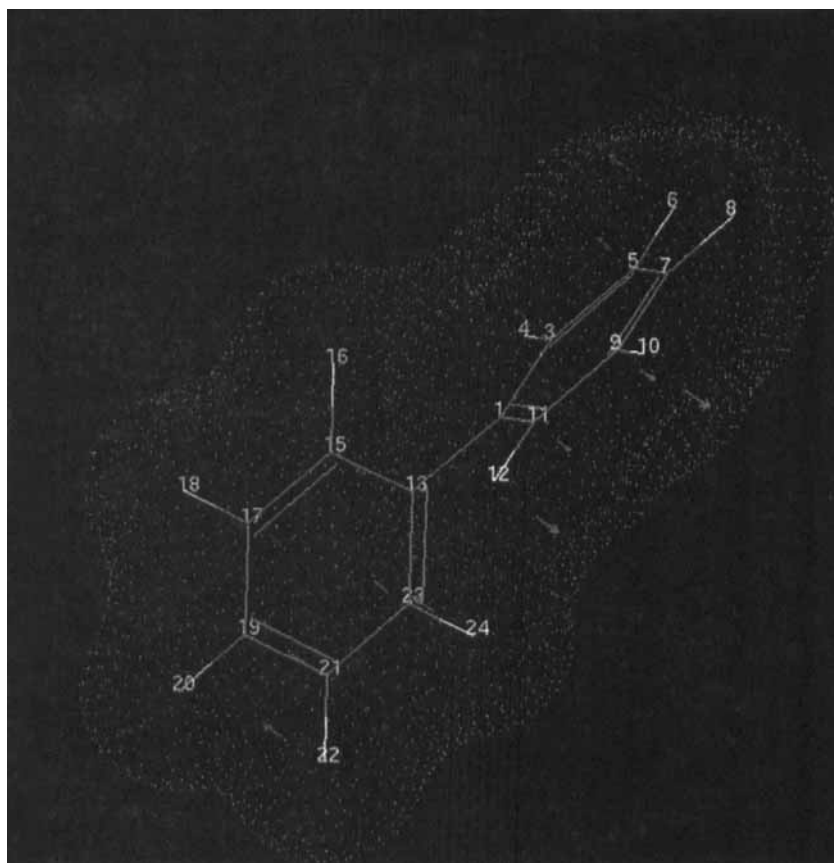


FIGURE 1 Graphical representation of biphenyl. (See Color Plate VI).

At this stage and given the limitations in computing facilities, the size of the systems to be dealt with precludes the use of significantly more extended basis sets or of methods taking electron correlation effects explicitly into account. In particular, since the aim is at the computation of vibrational properties, the neutral systems were treated as conventional closed-shell systems. All computed equilibrium structures were optimized under the constraints of (a) planarity and (b) all-anti conformations of the pyrrole units. Thus, the even-membered oligomers display  $C_{2h}$  symmetry, and the odd-membered oligomers display  $C_{2v}$  symmetry.

At the PM3 and AM1 level, the structures of both the benzenoid and quinonoid series of oligomers were determined up to  $n=5$ . The force fields, the vibrational spectra, and the vibrational intensities were evaluated for

TABLE III Table showing the geometry of the atoms in the bipyrrole derived from MOPAC using 3-21 G, PM3, AM1

<i>Atom</i>	<i>Bond length/X Å (3-21 G)</i>	<i>Bond length/X Å (PM3)</i>	<i>Bond length/X Å (AM1)</i>	<i>Atom</i>	<i>Atom</i>	<i>Atom</i>
C3	1.367	1.362	1.370	N4		
C14	1.439	1.438	1.440	C3	N4	
C13	1.361	1.362	1.360	C14	C3	N4
C12	1.359	1.360	1.360	N13	C14	C3
C11	1.395	1.397	1.400	C12	N13	C14
C10	1.401	1.401	1.400	C14	N13	C3
H15	0.951	0.950	0.950	C10	C14	C11
H16	0.949	0.950	0.950	C11	C12	C10
H47	0.951	0.951	0.950	C12	N13	C11
H17	0.899	0.900	0.900	N13	C14	C12
C2	1.398	1.401	1.400	C3	N4	C14
C1	1.392	1.394	1.395	C2	C3	N4
C5	1.359	1.360	1.360	N4	C3	C14
C5	1.359	1.360	1.360	N4	C3	C14
H9	0.949	0.950	0.950	C5	N4	C1
H6	0.951	0.950	0.950	C1	C2	C5
H7	0.948	0.950	0.950	C2	C3	C1
H8	0.898	0.900	0.900	N4	C3	C5

TABLE IV Table showing the bond angles of the atoms in the bipyrrole derived from MOPAC using 3-21 G, PM3, AM1

<i>Atom</i>	<i>Bond angle/Y° (3-21 G)</i>	<i>Bond angle/Y° (PM3)</i>	<i>Bond angle/Y° (AM1)</i>	<i>Atom</i>	<i>Atom</i>	<i>Atom</i>
C14	126.11	126.14	126.1	C3	N4	
C13	125.96	126.03	126.0	C14	C3	N4
C12	110.11	109.37	109.4	N13	C14	C3
C11	108.29	108.36	108.4	C12	N13	C14
C10	107.88	107.92	108.0	C14	N13	C3
H15	126.11	126.33	126.3	C10	C14	C11
H16	126.50	126.52	126.5	C11	C12	C10
H47	125.33	125.82	125.8	C12	N13	C11
H17	125.19	125.21	125.2	N13	C14	C12
C2	107.89	107.92	107.9	C3	N4	C14
C1	107.23	107.31	107.3	C2	C3	N4
C5	109.25	109.36	109.4	N4	C3	C14
H9	125.87	125.84	125.9	C5	N4	C1
H6	126.51	126.48	126.5	C1	C2	C5
H7	126.41	126.35	126.3	C2	C3	C1
H8	125.11	125.33	125.3	N4	C3	C5

simulations where *n* was up to 5 for the oligomers, Figure 2. Because the number as well as the size of the molecules treated in this work are too large to report all the various computed equilibrium structures, vibrational frequencies and vibrational intensities, we restrict the discussion to the most



TABLE V Table showing the comparison between experimental and simulated torsional angles of the atoms in the bipyrrrole derived from MOPAC using PM3

<i>Experimental torsional angle/Y° (PM3)</i>		<i>Simulated torsional angle/Z° (PM3)</i>		<i>Atom</i>	<i>Atom</i>	<i>Atom</i>
<i>Atom</i>				<i>Atom</i>		
N4				N4		
C3				C3	N4	N4
C14				C14	C3	N4
C13	− 180.0	− 179.0		N13	C14	C3
C12	− 180.0	− 180.0		C12	N13	C14
C11	0.1	0.0		C14	N13	C3
C10	180.0	180.0		C10	C14	C11
H15	− 180.0	− 180.0		C11	C12	C10
H16	180.0	180.0		C12	N13	C11
H47	180.0	180.0		N13	C14	C12
H17	180.0	180.0		C3	N4	C14
C2	180.0	180.0		C2	C3	N4
C1	0.1	0.0		N4	C3	C14
C5	− 180.0	− 180.0		C5	N4	C1
H9	180.0	180.0		C1	C2	C5
H6	− 180.0	− 180.0		C2	C3	C1
H7	− 180.0	− 180.0		N4	C3	C5
H8	− 180.0	− 180.0				

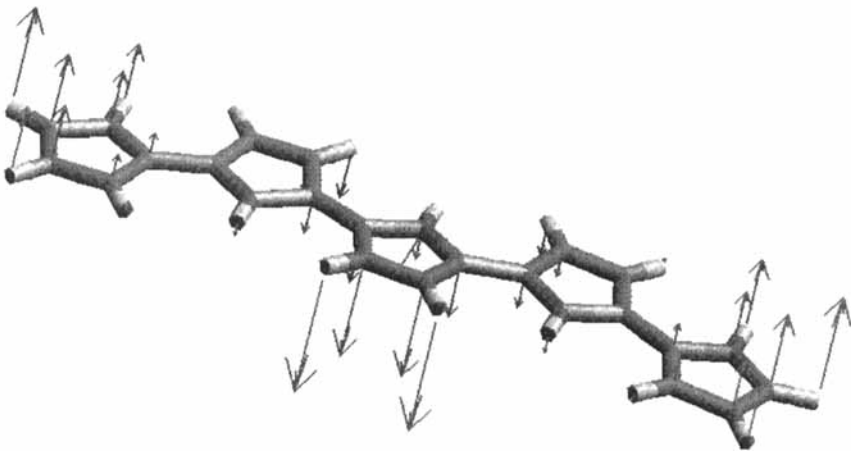


FIGURE 2 Schematic representation of the vibrational motions of polypyrrole with five sub-units. The mode animated is the 1509 cm<sup>−1</sup> mode of intensity 985.5 km/mol from the PM3 calculation (Tab. VII). (See Color Plate VII).

important vibrational spectroscopic trends in the three series occurring upon chain length elongation. Hence the evolution and the origins of the most intense bands in these series are discussed and the substantial differences between the two neutral series is stressed.

## RESULTS AND DISCUSSION

### Semi-empirical Calculations on the Structural and Electrical Properties of Poly(*p*-paraphenylene), PPP

Because of insolubility of PPP, vibrational spectroscopic techniques have been widely used for its characterization. The experimental vibrational spectrum of PPP [14] is illustrated in Figure 3. No transmittance values are given in this paper.

The characteristic vibrational absorptions of PPP were located around 650–900  $\text{cm}^{-1}$ . The absorption peak at 805  $\text{cm}^{-1}$  is due to the out of plane C—H vibration of poly(*p*-phenylene), the absorption peaks that appeared at 690 and 754  $\text{cm}^{-1}$  were attributed to the out of plane deformation of the C—H groups of benzene rings. On the other hand, the peaks at 2854 and 2992  $\text{cm}^{-1}$  indicated that the PPP was not completely aromatized, for these peaks were attributable to the C—H stretching vibration of alkanes.

Vibrational spectroscopy has also been employed for approximate molecular-weight determinations. Vibrational absorption band intensities and frequencies have been used as a base for a theoretical study of the electronic structure of PPP [14]. More recently, vibrational spectra have been used in comparisons of PPP samples prepared by different routes [15–17]. Information regarding structural changes in PPP brought about by doping with electron donors or acceptors [15]. The ratio of mono to *para*

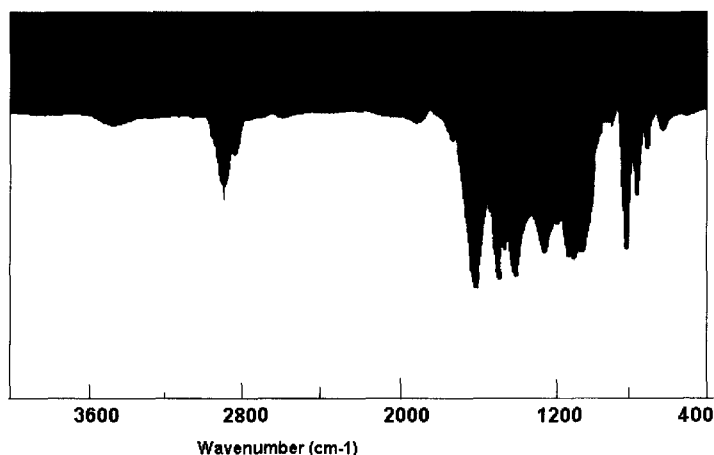


FIGURE 3 Vibrational spectrum, obtained from a KBr disk, of the experimental poly(*p*-phenylene).

disubstituted C—H out-of-plane absorption band intensities and the frequency of the *para* band in the vibrational spectrum can tell a lot of information about the conductivity of the molecule.

In this simulation (using MOPAC), Figure 4, the vibrational spectrum looks similar to the experimental one, even if the intensities were not reproduced due to the fact the experimental one was not giving a lot of information about intensities (Tab. VI). We can see the *para* band in it, but because in our model the structure is fully aromatic, peaks from impurities like those at  $2854$  and  $2922\text{ cm}^{-1}$  cannot be observed. The band gap is an important factor in determining electrical properties such as electrical conductivity, which is, to the simplest possible approximation, the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). If the magnitude of the band gap becomes smaller, the electrical conductivity increases.

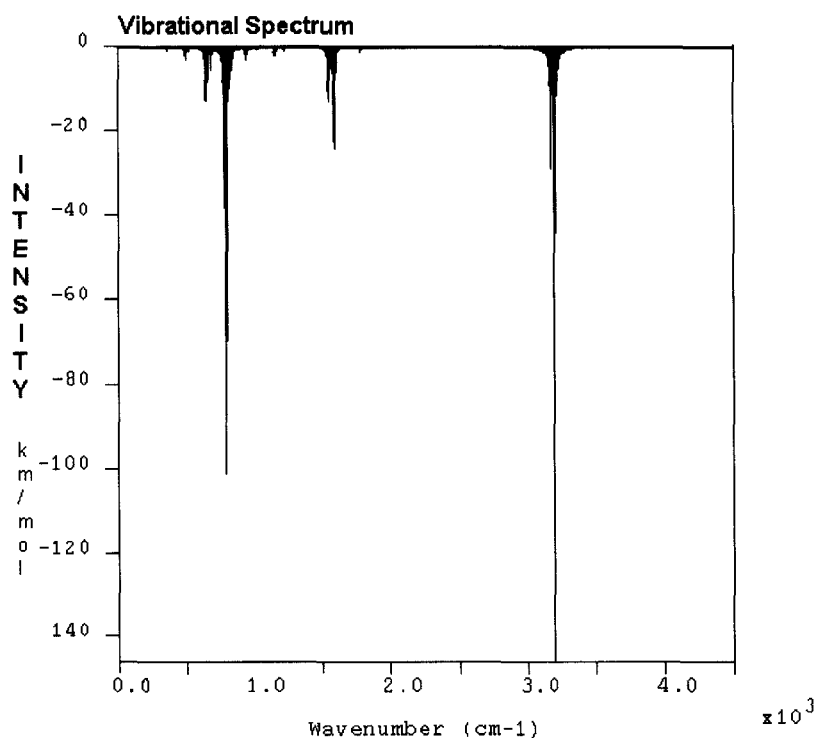


FIGURE 4 Vibrational spectra of (both IR and Raman active modes are shown) the simulated poly(*p*-phenylene) with a lorentzian peak shape fit.

TABLE VI Table comparing experimental and simulated vibrational data from MOPAC of poly(*p*-phenylene) highest intensity modes are underlined

Vibrational intensity km/mol	Wavenumber of simulated frequency by PM3 ( $\text{cm}^{-1}$ )	Wavenumber of experimental frequency ( $\text{cm}^{-1}$ )
16.0	645	
7.5	690.9	
146.7	<u>795.5</u>	<u>795</u>
10.7	<u>827.2</u>	<u>826</u>
34.4	1589.6	
75.5	—	2854
30.1	—	<u>2922</u>
11.5	3181.0	
13.2	3181.9	
13.8	3187.9	
23.4	3188.9	
72.6	3191.0	
91.6	<u>3191.9</u>	
69.5	<u>3201.1</u>	

The energy gap for the undoped aromatic form, the only one for poly(*p*-phenylene), was 7.9 eV, very close to undoped polypyrrole value of 5.1 eV. Doping the polymer will decrease the energy gap and enhance conductivity.

#### ***Ab initio* and Semi-empirical Calculations on Theoretical Vibrational Spectra of Polypyrrole**

The oligopyrroles are observed to converge quickly to the structural parameters of a minimised pyrrole ring [13]. This is a well-established, intimate relation between structural and vibrational spectroscopic properties, in particular between bond lengths and the corresponding stretching frequencies. Therefore the computation of vibrational spectra, which, for a given series ought to be converged with respect to further chain length elongation, requires the explicit treatment of very long oligomers. The structures of the quinonoid oligomers (*QnPPy*) converge almost as fast as that of the benzenoid oligomers. In 5PPy and in Q5PPy, the C—C bond lengths in the centre of the molecules have already converged to the same values. Analyzing the computed structures of benzenoid oligomers (*nPPy*) and quinonoid oligomers (*QnPPy*) it was observed that:

- (i) The bond length alternation is more pronounced in the *QnPPy* molecules than in their *nPPy* counterparts due to the greater 'double bond' character of the C—C bonds. (ii) The inter- and intra-ring C=C double bonds have essentially the same length in the quinonoid *QnPPy*, whereas the inter- and intra-ring C—C single bonds of *nPPy* differ at about 0.05 Å. In Tables III, IV and V, the C—C coordinates of 5PPy and

Q5PPy are compiled as they were obtained at the PM3 and AM1 and 3-21G level. Although the 3-21G results are more computationally expensive when compared to the AM1 and PM3 force fields, this set of hamiltonian coordinates exhibit a very similar behaviour. Therefore, the use of the PM3 for molecules too large to be treated with the 3-21G basis set appears to be justified. Because of the insolubility of polypyrrole, vibrational spectroscopic techniques have been widely used for its characterization. In Figures 5-6, the computed vibrational line spectra of the *n*PPy and *Qn*PPy for *n*=5 are displayed from calculations using the AM1 and PM3 methods.

The theoretical vibrational spectra of the *n*PPy series converge nicely with each other at increasing chain length, at least as far as the frequencies are concerned, Table VII.

The intensity ratios also converge well when values of *n* are greater than 5. With increasing oligomeric length, the intensities of the bands around 800 cm<sup>-1</sup> increase relative to that of the strong band slightly below 700 cm<sup>-1</sup>,

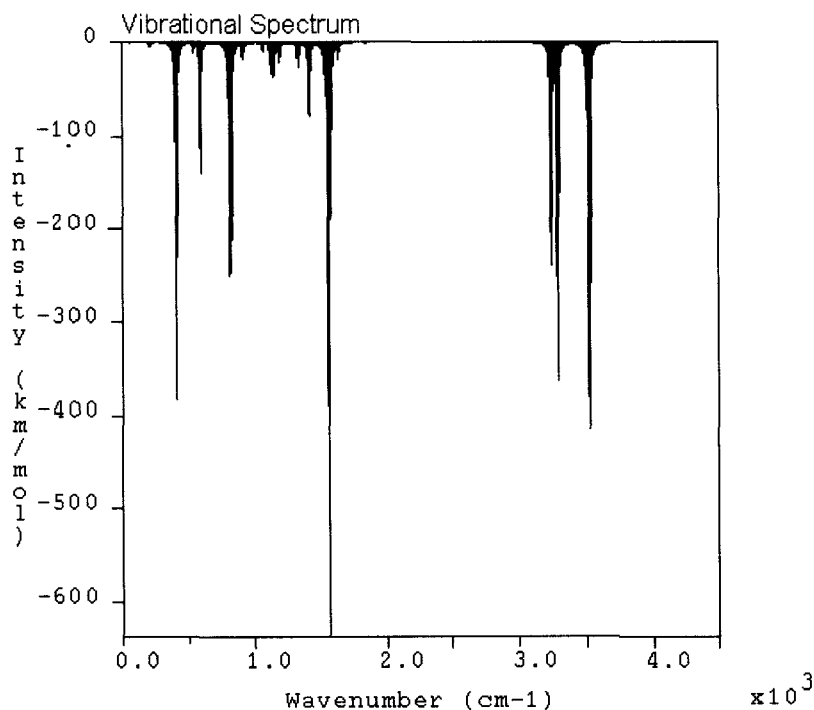


FIGURE 5 Vibrational spectra (both IR and Raman active modes are shown) of a simulated polypyrrole in the benzenoid form with five sub-units using AM1 method.

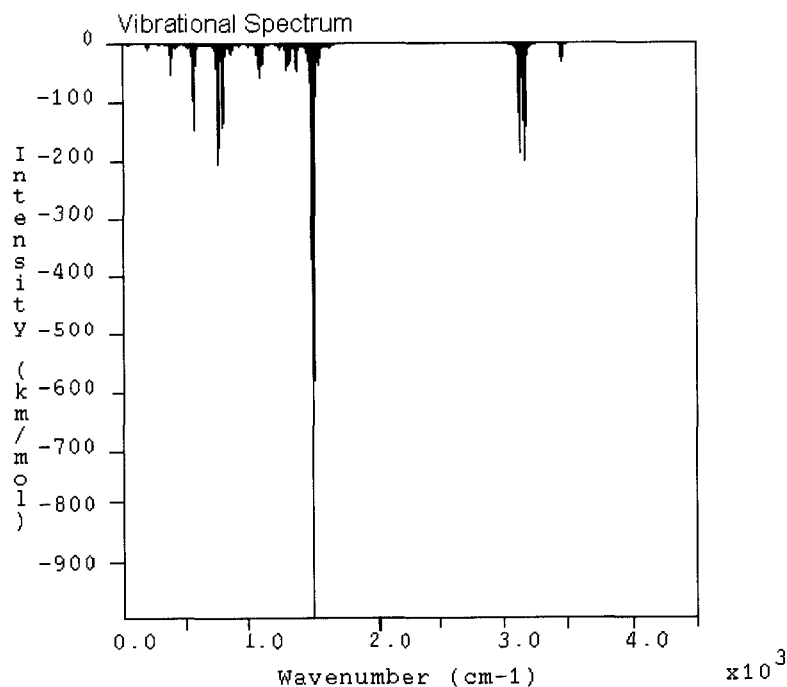


FIGURE 6 Vibrational spectra (both IR and Raman active modes are shown) of a simulated polypyrrole in the benzenoid form with five sub-units using PM3 method, Figure 2 shows the animation of the highest intensity mode.

TABLE VII Table comparing AM1 and PM3 simulated vibrational data of benzenoid Polypyrrole (five sub-units) highest intensity modes are underlined, the schematic representation is shown in Figure 2

<i>Vibrational intensity km/mol</i>	<i>Wavenumber of simulated frequency by AM1 (cm<sup>-1</sup>)</i>	<i>Wavenumber of simulated frequency by PM3 (cm<sup>-1</sup>)</i>
397.8	<u>412</u>	
156.7		575
149.7	598	
137.8		764
149.3		801
210.3	811	
228.3	824	
156.9		<u>1504</u>
985.5		<u>1509</u>
637.9	<u>1565</u>	
103.2		3122
96.3		3124
117.3	3241	
230.7	<u>3293</u>	
250.8	<u>3528</u>	
148.2	<u>3537</u>	
217.1	3538	

all of them originating from C—H out-of-plane bending motions. The latter already dominates the pyrrole spectrum, and its intensity remains approximately constant over the whole series. The bands in the vicinity of  $1400\text{--}1600\text{ cm}^{-1}$  also gain in intensity upon chain length elongation. All these features occur in the experimental vibrational spectra reported by Kofraneck *et al.* [3]. The differences between the the AM1 and PM3 methods are noted in the density of the vibrational peaks as well as the number. In the AM1 case the intensities for all the cases are low and the peaks are quite widely spread unlike the PM3 in which we have a few values but in much higher intensities.

Overall, a quite similar behaviour is found for the QnPPy series. The relative IR intensities and the computed frequencies of the vibrational modes do not change much with increasing chain length, although the absolute vibrational intensities increase. In this region, intense IR bands at  $3500\text{--}3000\text{ cm}^{-1}$ ,  $1400\text{--}1600\text{ cm}^{-1}$ ,  $1209\text{ cm}^{-1}$ ,  $900\text{--}880\text{ cm}^{-1}$  and  $776\text{ cm}^{-1}$  for the QPPy molecule are predicted. From Table VI it can be seen that: (i) Convergence of the PM3 and AM1 results is almost achieved with  $n=5$ , and (ii) the PM3 and AM1 results are surprisingly close to the *ab initio* results and may be helpful at least for a qualitative understanding of the IR intensities in longer polymers. For the neutral oligomers, strong IR intensities are obtained at the PM3 level.

## CONCLUSIONS

In this paper computational techniques, *i.e.*, *ab initio* and semi-empirical methods, were used to calculate the theoretical spectra and structural parameters of energy minimised conducting polymers and compare with experimental data from the literature. Phenylene and Pyrrole are promising molecules for conductivity studies of polymers by computational and experimental techniques due to the nature and linearity of their conjugated backbones. The literature vibrational values for the conducting poly(*p*-phenylene) and polypyrrole were very close to the modelling ones. One explanation could be that *ab initio* and semi-empirical parameters and the force fields derived from them models these molecules well and the amount of simulation time for these specific linear polymers was adequate. Computer simulation techniques are clearly now able to provide valuable insight as to the structure and properties of polymers at the atomic level. Future developments are likely to include the extension of electronic-structure techniques to larger and more complex systems.

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