



DFT study of structural, vibrational and electronic properties of polyaniline pernigraniline model compounds



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ABSTRACT

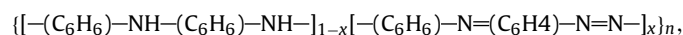
Polypernigraniline is the only polyaniline to possess a doubly degenerate ground state. In the present work using density functional theory (DFT) calculations, the structural, vibrational and electronic properties of two well-known model compounds of polyaniline pernigraniline have been investigated. A detailed vibrational analysis of phenyl-end-capped dimer (B2Q1) and phenyl-end-capped tetramer (B3Q2) have been presented and complete assignments are reported. Lower region spectral assignments which were not being reported earlier are being done in the present work. DFT calculations with 6-31G** basis set produces very good results of IR and Raman spectra allowing better understanding of these compounds. TD-DFT calculations for HOMO–LUMO analysis give insights into the electronic structure of these model compounds.

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1. Introduction

In the conducting polymers field, polyaniline (PANI) is one of the most studied substance during past few decades, in particular, because of its good environmental stability [1,2], cost effectiveness, ease of synthesis [3], processing [4] and controllable electrical conductivity [5]. This very important polymer has applications in various field of life, viz. in catalysis [6–8], energy storage [9,10], battery electrode material [11], drug-delivery [12,13], sensors [14], solar and fuel cells [15,16], supercapacitors [17], as an electrochromic–display material [18] and as a material for removal of water pollutants [19,20]. On the contrary, only few works were devoted to the related oligomers. During past few years there has been increased research interest on PANI oligomers and model compounds [21–25]. Model compounds and oligomers provide the opportunity to design and produce synthetically well-defined and well-characterized species with defined functionality and properties [26,27]. Also, actual samples of conjugated polymers have more or less disordered structures and a distribution of conjugation lengths. Thus, spectroscopic studies of well-defined model compounds are useful for a better understanding of different properties of conducting polymers [28].

Several forms of polyaniline can be obtained by tuning two parameters: the average oxidation state [29,30] and the degree of protonation [5,31]. Polyaniline differs structurally from other conducting polymers, as its electronic properties depend upon nitrogen hetroatom doped between constitutional phenyl (C₆H₆) rings in the backbone allowing chemical flexibility to access several oxidation states. The general formula describing PANI chain is



where x gives the average degree of oxidation. The three stable forms of PANI correspond to the values $x = 0$ (leucoemeraldine base, LB), $x = 0.5$ (emeraldine base, EB), and $x = 1$ (pernigraniline base, PNB).

The study of oligomeric compounds as a tool to understand the structure and behavior of polyaniline forms has been the subject of a number of papers [32–40]. A detailed vibrational analysis with dynamical or quantum chemical calculations of oligomers with precisely defined length and constitution has shown to provide information not only about the molecular vibrations of the compounds under study and the corresponding polymeric chain but also about their electronic configuration [41–44]. Vibrational spectroscopy is extremely sensitive to the electronic structure changes in polyaniline. Thus by using infrared and Raman, one can easily register all interconversions between different states of polyaniline involving both oxidation and protonation processes.

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Recently a great number of quantum mechanical research is devoted for studying structure and electronic properties of conducting polymers. The application of quantum chemistry methods to polymers are generally limited by size, complexity and computing time. Recently, density functional theory (DFT) calculations have become useful for predicting molecular geometries, energy levels, and absorption spectra of conjugated organic molecules [45–50]. Performing DFT calculations on conjugated polymers is challenging due to their size (large number of atoms), however, they can be approximated using oligomeric model compounds [51–53].

As we know that HF calculations tend to overestimate the frequencies of different modes, and this tendency cannot be eliminated by the standard scaling procedures [54,55]. However, situation can be improved if we include DFT because density functional calculations can include electron correlation with modest computational cost. Generalized gradient approximation (GGA) is an appropriate method for simulating vibrational spectra of finite and infinite number of atoms. Clavaguera-Sarrio et al. [56] reported that the GGA can successfully predict the structural and vibrational properties of closed and open-shell systems for oxides of actinide compounds. Also, recently Adjokatse et al. [57] found a very nice correlation between theoretically simulated vibrational spectrum and experimental results for Nylon-7 using plane-wave pseudopotential basis and GGA calculations. Both the GGA and hybrid B3LYP are quite effective at simulating the vibrational spectra of polymers, however the latter is more abundantly used in the literature in case of conducting polymers including polyanilines [58,59]. The vibrational frequencies calculated with appropriate functionals are often in good agreement with the observed frequencies when the calculated frequencies are uniformly scaled with only one scaling factor [60,61]. However there are few papers where dual scaling factors have reasonably produced good results [62,63].

The PNB form of PANI has attracted significant interest because it is the only known polymer besides polyacetylene that is known to exhibit a two-fold degenerate ground state [64–66]. In continuation to our recent works on PANI–PNB [67,68], in the present work I have determined the geometric, vibrational and electronic properties of PANI–PNB form model compounds using density functional theory. In the present work, I have made the normal coordinate calculations on two well-known model compounds of polyaniline pernigraniline base form, phenyl-end-capped dimer (B2Q1) and phenyl-end-capped tetramer (B3Q2) and calculated their IR and Raman spectra. A detailed comparison with the observed infrared (IR) [69,70] and Raman spectra [69,70] is reported. Assignments are made on the basis of the Raman and IR intensities, atomic displacements of vibrational modes and calculated potential energy distribution (PED) of each vibrational mode. The frontier energy levels of conjugated polymers are important parameters for optimizing materials for organic electronic applications. Using TD–DFT calculations, HOMO and LUMO orbitals of these two model compounds have been interpreted.

2. Computational methods

The DFT calculations have been performed with the Gaussian 03 program [71] and analyzed with the help of the Gauss-View program [72]. The geometries of the model compounds are fully optimized i.e., without any physical constraint or forced symmetry using the 6-31G** split-valence basis set, at the DFT level. Calculations are mainly carried out in the frame-work of the Becke–Lee–Yang–Parr [B3LYP] functionals, in which the exchange functional is a local spin density exchange with Becke gradient correction [73] and the correlation functional is that of Lee Yang, and

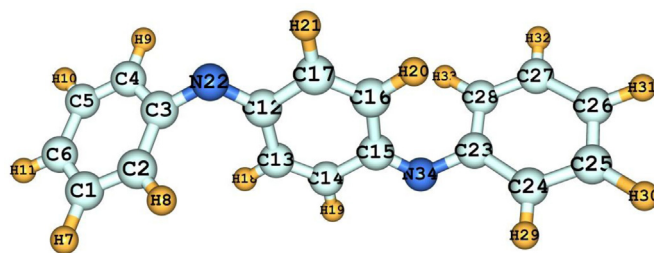


Fig. 1. B3LYP/6-31G** optimized geometry of B2Q1.

Parr with both local and non-local terms [74]. Convergence criterion in which both the forces and displacement are smaller than the cut-off values of 0.00045 and 0.0018 and r.m.s force and displacement are less than 0.0003 and 0.0012 have been used in the calculations.

Quillard et al. [69] and Cochet et al. [70] synthesized polyaniline in a form of emeraldine hydrochloride by oxidative polymerization using ammonium peroxodisulfate following the procedure of MacDiarmid et al. [75]. In their work [69,70], Fourier transform (FT) Raman spectra (Bruker RFS 100 FT Raman spectrometer) and Infrared spectra (Nicolet 20 SXC FT infrared spectrometer) together with force field calculations were used for vibrational analysis of different PANI model compounds. In the present work, the absolute Raman scattering and IR absorption intensities are calculated in the harmonic approximation at the same level of theory as used for the optimized geometries. The normal mode analysis is being performed and the potential energy distribution [PED] is calculated along the internal coordinates using localized symmetry [76,77]. In the present work all the calculated frequencies are scaled with a common scaling factor of 0.9613 [60,61]. Vibrational assignments of the normal modes are being done on the basis of the band profile, intensity and PED, calculated using GAR2PED program [78]. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are plotted using computer program Gauss-View [72].

3. Results and discussion

The molecular structures of the two model compounds B2Q1 and B3Q2 of PANI–PNB form is discussed in this section, followed by the discussion of vibrational assignments and electronic structure of these two model compounds.

3.1. Geometric structure

In the present work, first model compound studied is B2Q1, in which there is one quinoid (Q) ring in between two benzoid (B) ring and second model compound is B3Q2, where there are two quinoid (Q) and three benzoid (B) rings. Before performing vibrational analysis first a detailed structural analysis is performed on both model compounds. The total torsional angle between the phenyl rings is one of the main important factors that govern the band-gap in the polyaniline family of compounds [79,80]. From the DFT structural analysis of these two model compounds, I found that torsion angle between terminal benzoid ring and quinoid ring is around 58° for both model compounds. As the number of rings increases in B3Q2, the torsion angle in middle decreases to ~55°, which was found to be around 51° for PANI–LB in our earlier DFT study on PANI–LB model compounds [59]. Figs. 1 and 2 show the DFT relaxed structure of these two model compounds. All the optimized bond lengths, bond angles and dihedral angles are given in Tables 1 and 2 for B2Q1 and B3Q2, respectively.

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