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DFT modeling of polyaniline: A computational investigation into the structure and band gap of polyaniline.

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Abstract

The band gaps of three forms of polyaniline (PANI) are calculated using the DFT method with the B3LYP functional and SV(P) basis set. This marks the first time that the band gap for this polymer has been calculated using this DFT method. The calculations include an investigation of the effect of varying the benzoid-quinoid structural units, the effect of increasing oligomer length and the inclusion of Michael's addition structures which could be residual in the polymer depending on the chosen synthetic method. All results were compared to the experimentally determined band gap of 1.5 eV as typically reported in the literature. A commonly used structural motif of alternating benzoid-quinoid units and a ratio of 0.5:0.5 benzoid: quinoid resulted in a computed band gap of 1.9 eV. Inclusion of one extra quinoid unit gave rise to a band gap of 1.3 eV. Incorporation of a Michael's addition structure was found to dominate the band gap calculation, yielding a localized LUMO and a band gap of 1.3 eV that was insensitive to the polymer chain length and composition.

Keywords: Polyaniline, B3LYP/ def sv(p), band gap, computational chemistry, TurboMol

1 Introduction

Polyaniline is an intrinsically conductive organic polymer. It is one of the more robust of the organic conductive polymers, as it is air stable and convenient to synthesize. Polyaniline has found a wide range of uses including as a hole injection layer on organic photovoltaic cells¹, supercapacitors^{2,3} and biosensors⁴. One of the areas of interest to our research group is the application of polyaniline as a sacrificial anode in corrosion resistant materials^{5,6}. The narrower the band gap, which is the difference in energy between the conduction band and the valence band of a material, the more likely the material is to be conductive. In turn, the more conductive the material is, the better a sacrificial anode it makes in a corrosive environment. As such, the width of the band gap of polyaniline can reflect both the conductivity of the material and the likelihood of it being effective as a sacrificial anode. It should be noted that polyaniline is known to be an effective corrosion suppression agent added to sol-gel systems, when applied at sufficiently high concentrations to a metal substrate such as low carbon steel⁷. Though the exact nature of its anticorrosive action is not well described, scientists suspect that polyaniline works as a sacrificial anode⁸ due to its narrow experimental band gap of 1.5eV.⁹ What is not known is how the structure of polyaniline relates to the narrow band gap of the as-synthesized material. The structure of polyaniline is typically represented by that shown in Fig 1.

Fig. 1 Proposed structure of polyaniline in the emeraldine base form

This polymer form is conductive and is referred to as the emeraldine base. It contains repeating benzoid (blue) and quinoid (red) units. The polymer can also exist as a fully reduced form, leucoemeraldine, which is comprised of all benzoid groups (Fig 2. blue) and a fully oxidized form called perigraniline, comprised of all quinoid groups (Fig 2. red).

Fig. 2: Structures of leucoemeraldine (left, blue) and perigraniline (right, red)

As expected, the structures and conductivities of the various forms of polyaniline are related, with leucoemeraldine being insulating and the emeraldine base being conductive¹⁰. The exact structure of the emeraldine base has not been determined, but X-ray photoelectron spectroscopy (XPS) confirms the presence of benzoid and quinoid units¹¹. X-ray diffraction studies performed by Pouget et al.¹² have

shown that the typical polymer morphology is planar. However, due to the amorphous nature of the polymer and very few reflections in the X-ray diffraction data, they were not able to determine a more complete crystal structure of the material, a problem that exists to this day.

Computationally, previous literature has explored the canonical structure shown in Figure 1 with a balance of benzoid and quinoid structures^{9,13}. While this is an appealing starting point, our work demonstrates that the inclusion of heterogeneity in the PANI structure being modelled is key to accurately determining its band gap and therefore essential for understanding the structure most relevant for its possible applications. This includes investigation of the impact length of the polymer chain, the benzoid:quinoid ratio and the inclusion of synthetically relevant structures containing different heteroatoms. In short, the calculations must be informed by the nature of the synthetic products to ensure the most meaningful computational outcomes.

There are two general ways of synthesizing polyaniline: electrochemically, using aniline and a current¹⁴, or chemically, using ammonium persulfate and aniline at a low pH¹⁵. The electrochemical method of synthesizing polyaniline should create discreet domains of alternating benzoid-quinoid units. This means that a strict adherence to regular benzoid-quinoid alternation may not be the most accurate representation for the starting point for computational modelling. Alternative structures must be evaluated, and the inclusion of particular structural elements must reflect the chemical method used to synthesize the polymer.

A common method for the synthesis of the emeraldine base uses aniline and ammonium persulfate as the oxidant. This ammonium persulfate method produces a polymer that contains alternating benzoid-quinoid units but also includes a Michael addition product that contains oxygen, carbon, hydrogen, and nitrogen¹⁶, as well as a sulfur-containing compound. The Temperini group¹⁶ have been one of the few groups to thoroughly investigate the structures formed from polyaniline synthesized using this method at low pH with characterization using Raman, NMR, FTIR and UV-vis-NIR spectroscopy. Their

work suggests that that the polymer contains some 1,4-Michael's addition adducts (Fig.3) in addition to the repeating benzoid-quinoid units shown in Fig.1.

Fig. 3: Michael-type adduct proposed by Temperini et al¹⁶.

In addition to consideration of the departures from the canonical PANI structure, this work also relied entirely on the DFT computational method for determining the properties of the structures. Previous work has utilized the semi-empirical method¹³, crystal structure restrictions¹⁷ or the use of periodic boundary calculations¹⁸. The latter of has been used as a more straightforward method of obtaining the band gap of certain polymers¹⁸ compared to the previously employed method of extrapolation of the HOMO-LUMO gap energies after a single DFT calculation on short chain oligomers⁹. With the advent of programs such as TURBOMOLE¹⁹ and its ability to perform DFT calculations of larger structure, it is now possible to determine the relationship between the band gap of the polymer and its structure without the use of semi-empirical methods or computational power savers such as crystal structure restriction, or periodic boundary conditions, allowing for a more precise determination of the factors influencing the electronic properties of polyaniline.

Previous computational research into PANI has used semi-empirical methods to optimize the structure of the emeraldine base and determine the band gap of the polymer. Chance et al.¹³ used semi-empirical calculations to optimize the structure of the emeraldine base and determine the band gap of the polymer using the Valence Effective Hamiltonian method. Kwon et al.⁹ used the B3LYP DFT method to optimize the structure of a three-unit oligomer of aniline.

This work describes our investigation into the relationship between the structure and conductivity of polyaniline in which we use the B3LYP DFT method to calculate the HOMO-LUMO gap of the material starting with one aniline unit and extending the polymer chain using alternating benzoid-quinoid units until the HOMO-LUMO gap converges as a function of chain length. Heterogeneities in the canonical structure are then introduced and their significant impacts on the band gap are identified.

2 Method

The TURBOMOLE (Karlsruhe, Germany, www.turbomole.org) program¹⁹ has been used for the calculations, employing the B3LYP DFT method²⁰ with the basis set def-SV(P)^{21–23}. This functional corresponds to Becke's three-parameter hybrid exchange and to the Lee-Yang-Parr's correlation functionals. B3LYP/def-SV(P) was selected as a good balance between computational rigour and reasonable CPU demand. The final band gap of the emeraldine base with a ratio of 0.5:0.5 benzoid to quinoid units, referred to as the EB system, was obtained by convergence of the HOMO-LUMO gap as a function of chain length. The typical calculation methodology was as follows: aniline was geometry optimized using B3LYP/def-SV(P) and then benzoid and quinoid units were added and geometry optimized successively. HOMO-LUMO gap energy changes of less than 0.02 eV with subsequent additions of benzoid or quinoid units was used as the indication of convergence.

Due to the lack of congruity between the band gap of the 0.5:0.5 benzoid-quinoid unit structure and the experimental band gap value, a variation of the structure of the emeraldine base was made by placing a quinoid unit next to another quinoid unit on the growing polymer chain, referred to as EB-QQ

for emeraldine base-quinoid-quinoid. This was done after the addition of the fifth quinoid unit on the polymer chain. The band gap of this system was obtained as previously described.

In order to explore the effect of incorporation of a Michael adduct inclusion in the PANI backbone as has been demonstrated experimentally when PANI is synthesized using APS, the calculations were performed as follows: The band gap of the 1,4-Michael adduct (Fig.3) was calculated using B3LYP def SV(P), then successive benzoid and quinoid units were added onto the terminal amine group of the adduct. The HOMO-LUMO gap energy was calculated for each structure. Similarly, 3,3-sulfonyldianiline was added to the adduct modified PANI structure and the HOMO-LUMO gap of the compound with five quinoid units and both heteroatom inclusions was calculated. Successive benzoid and quinoid units were then added and the HOMO-LUMO gap of each of these units were calculated until the calculated band gap value converged.

3 Results and Discussion

3.1. Band gap of the EB polymer

The first step in this work was to determine if the B3LYP DFT method could accurately determine the band gap of an emeraldine base polymer without restrictions on the structure of the polymer⁹ or boundary conditions¹³.

The first structure was an emeraldine base with repeating benzoid-quinoid units using a 0.5:0.5 benzoid:quinoid ratio. As shown in Fig. 4, the HOMO-LUMO gap of the structure decreases steadily with each monomer addition down to a value of 1.9 eV, after the addition of the seventeenth repeating benzoid quinoid unit. Subsequent additions do not result in a continued decrease of the calculated band gap. Using this homogeneous, alternating, canonical structure, 1.9 eV is the closest approach to the experimentally measured band gap of 1.5 eV⁹.

1

Fig.4: Graph the Band Gap of the EB system (square) and the EB-QQ system (circle) the number of the aniline units

The DFT calculated band gap of 1.9 eV is higher than band gaps calculated using other methods. Kwon et al⁹ determined a band gap of 1.3 eV for the EB system using the semi-empirical method that is not parameterized for the quinoid units of polyaniline. However, this is the first time that a DFT method has been used to determine the band gap of polyaniline. It should be noted that the DFT method has been used to accurately determined the band gap of other conductive polymers^{24–26}, and has been found to be more accurate than the semi-empirical method.²⁷ Therefore it is safe to assume that the result of 1.9 eV for the band gap of the commonly displayed structure of polyaniline is in fact a more accurate representation of the band gap for this material. If this is true, this means that the homogeneous alternating canonical structure of polyaniline is not the most accurate structure of the polymer. To explore this computationally, the band gaps for a series of less homogeneous structures were determined by DFT.

Visualization of the HOMO orbitals of this EB polymer shows, as expected, a delocalization of the HOMO orbitals along the chain of the structure suggesting that the electron density is distributed evenly along the polymer chain and that this structure is conjugated, lending veracity to the fact that this is a plausible structure of polyaniline. Even though the structure is conjugated, as one might expect, this structure does not have a narrow HOMO-LUMO gap and is not the correct structure of polyaniline (See supporting information). Visualization of the LUMO orbitals shows localization of the quinoid structure of the material suggesting that the quinoid structure plays a vital role in the formation of the band gap. This is also supported by the large change in HOMO-LUMO gap energy when the first quinoid unit is added to the growing chain (Fig.4).

3.2 The Band gap of the emeraldine base with a quinoid-quinoid (EB-QQ) inclusion

Previous researchers have characterized electrochemically synthesized PANI and identified a 0.75:0.25 benzoid: quinoid ratio²⁸. So, this ratio was calculated, and the results were identical to the previously described 0.5:0.5 ratio with a band gap of 1.9eV, suggesting that increasing the benzoid content of the polymer did not change the band gap.

Since the increase in benzoid content did not change the band gap, a structure based on the information provided from the X-ray structure determined by Pouget et al.¹² was used. Due to the challenges of collecting enough reflections for the PANI, the exact structure of polyaniline could not be determined. However, Pouget and co-workers proposed that polyaniline had a constant repeating bond angle and bond lengths (Table 1). For the purposes of building our structure, the key parameters used were that the C-NH₂ and the C=N bond lengths were the same (1.36 Å), not varying lengths (1.39Å and 1.31 Å respectively). The bond angles between the C-N=C fragment and the C-NH-C fragments were also kept at a constant 140.7°. This resulted in a more planar structure than the EB structure and the EB structure with a 0.75:0.25 ratio of benzoid to quinoid. The band gap was formed after the addition of 5 repeating benzoid-quinoid units and was 1.1 eV, which is not in good agreement of the experimental value of 1.5 eV. Given that the inclusion of more benzoid units and the inclusion of the X-ray structure

did not correct these differences in band gap, a structure with a higher ratio of quinoid units was examined.

Table 1: Bond lengths of the fragments in the X-ray structure representation of polyaniline¹².

Structural fragment	Bond Length (Å)
C-NH ₂	1.36
C=N	1.36
C=C	1.407
C-H	1.08

The preceding calculations demonstrated that the canonical structure is not the most accurate structure of polyaniline and demonstrate that the inclusion of more benzoid units does not improve the congruence between the calculated and experimental band gap. The previous calculations also show that making the structure more regular and more planar does not improve the congruence between the band gap and the experimental value. So, we are left to explore what the addition of more quinoid units would do to the calculated band gap of polyaniline. To explore the effect of irregularities in the repeating structure of the PANI backbone, band gap calculations were carried out on structures with variations in the benzoid-quinoid repeating pattern.

The EB-QQ system is very similar to the EB system except that it has two quinoid units next to each other at the fifth quinoid unit, after which benzoid-quinoid alternation resumes. This inclusion of an extra quinoid unit leads to a significant decrease in the band gap of the polymer from 1.9 eV to 1.3 eV as can be seen in the sharp downward curve in Fig. 4. The inclusion of just one excess quinoid unit brings the calculated band gap value into significantly better agreement with the experimental band gap of 1.5 eV.⁹ Previous work with the B3LYP DFT method has shown that a 0.2 eV difference between the experimental band gap and the calculated band gap is to be expected.^{24–26}

Visualization of the HOMO orbitals of the EB-QQ structure (See supplemental information) shows the localization of the HOMO orbitals on the growing chain of the polymer, demonstrating that the band gap is controlled by the growing chain of the polymer. Visualization of the LUMO structure (See

supplemental information) shows the centering of the LUMO orbitals around the quinoid quinoid defect structure of the polymer. This shows that the quinoid quinoid defect plays a role in controlling the band gap of the structure, which is supported by the HOMO-LUMO gap energy of the structure (Fig. 4). This result is in keeping with the work of Wong et al¹⁸ and the reviews by Xiaozhou et al²⁹ and Mikie and Osaka³⁰, who have all demonstrated that increasing the quinoidal character of a polymer leads to the decrease in the band gap of the material.

3.3 The Band Gap of the Michael's Adduct

Another potentially very important introduction of heterogeneity into the canonical PANI structure is the inclusion of Michael's adduct structures, which are particularly relevant for modeling chemically polymerized PANI. The motivation for the inclusion of this structure is found in both the literature and in the characterization of our own APS-based synthetic PANI. XPS elemental survey scan of a sample of our APS synthesized PANI is shown in Figure 5. The XPS clearly shows the expected C, N and O content consistent with the Michael's adduct in the PANI. The XPS also shows a sulphur content which is discussed separately below.

The HOMO-LUMO gap of the Michael's adduct structure (Fig.3) on its own, was calculated and was found to be 1.3 eV. This is in good agreement with the PANI experimental band gap of 1.5 eV⁹. Consecutive benzoid and quinoid groups were added to the structure and the HOMO-LUMO gap of the growing polymer was calculated. It was found that addition of aniline units to the Michael's adduct structure did not impact the HOMO-LUMO gap of 1.3 eV

Fig.5: The XPS survey scan of polyaniline made with Ammonium Persulfate

Analysis of the XPS data acquired for our APS synthesized PANI also identifies a consistent sulfur content of approximately 3 atomic percent. The sulfur species binding energy from the high resolution XPS spectrum indicates that the binding energy is consistent with the species SO_2 (Fig. 6). Previous work³¹ suggests that the SO_2 may be conjugated between two benzene rings. The oxygen fitting however, shows two distinct fitted peaks at 531.45 (C=O aromatic) and 533.06 eV ($\text{C}_6\text{H}_4\text{-SO}_2\text{-C}_6\text{H}_4$), which indicates that there are two distinct oxygen species; one that corresponds to the SO_2 and the other corresponding to an aromatic C=O. Both assignments support the presence of the Michael's adduct product and a sulfur containing species such as the one shown in Figure 7. The ratio of oxygen in these peaks to the atomic % sulphur and atomic % oxygen is in good agreement with the proposed sulphur species.

Fig.6: The high-resolution scan of the sulfur peak in the XPS

To evaluate the effect of the addition of sulfur to the polymer, 3,3-sulfonyldianiline was included in the growing chain of the polymer after the fifth quinoid unit. This was placed at this position so that the compounds could be consistent with the EB-QQ compound. The addition of the sulfur compound did not shift the band gap of the polymer.

Figure 7: The structure of 3,3-sulfonyldianiline

Fig.8: The electron density of the Lowest Unoccupied Molecular Orbital on the Michael's adduct oligomer

Further examination of the electronic structure of the PANI including the proposed heterostructures (Fig.8) shows that the electron density of the polymer created in this way is centered around the adduct and not around the growing polymer chain. This suggests that the band gap of the material is dominated by the adduct and not influenced by the polymer chain or the inclusion of the sulfur containing species. Therefore, the band gap will not change regardless of what is added to the material beyond the adduct. This implies that the conductivity of the polymer is controlled by the adduct, which means that polyaniline synthesized with APS can be conveniently modified to increase the workability of this intractable polymer as long as the adduct remains mostly changed. This is consistent with the results of the PANI band gap calculation when the adduct is included and demonstrates the importance of including key heterostructures that are dependent on the synthetic method used to make the actual polymer.

With a calculated band gap of 1.3 eV and nitrogen, oxygen, carbon, hydrogen and sulfur included in the polymer this structure could be a good candidate for the emeraldine base when ammonium persulfate is used as the oxidant and aniline is used as the starting material.

By understanding the relationship between the structure and band gap of polyaniline we can now accurately predict how modifications to the polyaniline backbone affect the conductivity of the polymer. As a result, it is possible to screen the modifications to polyaniline with the hope of narrowing the band gap and increasing its conductivity. An increase in its conductivity would allow this new polyaniline to act as a better corrosion suppression agent or as a better hole injection layer in photovoltaic cells.¹

4 Conclusion

Our work marks the first time that the band gap of this polymer was calculated using only a DFT method, which has been shown to be more accurate than any semi-empirical method previously employed. The results have shown that the highly homogeneous, canonical structure frequently used in computations of PANI is not sufficiently sophisticated to correctly describe the electronic properties of polyaniline. With respect to the EB-QQ structure, the band gap is formed after the addition of 17 units, which suggests that experimentally PANI could be used as a 17 unit oligomer for conductive polymer applications which could provide a convenient solution to the solution processing challenges that are often encountered when synthesizing and using PANI. The calculation of the band gap for the proposed EB-QQ structure also shows that changing the benzoid quinoid ratio in favour of a slight excess of quinoid units lowers the band gap substantially. Finally, the inclusion of synthetic-method specific heterostructures such as the Michael adduct in the backbone can dominate the calculated electronic properties and must be considered in both computational and experimental work.

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