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POLYANILINE: A THEORETICAL STUDY

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Abstract

Theoretical predictions for various neutral and charged forms of polyaniline are presented and discussed. The MNDO semiempirical method is used to predict geometries, which serve as input for Valence Effective Hamiltonian (VEH) calculations of the electronic band structure. The VEH calculations provide predictions for the band gaps, ionization potentials, electron affinities and redox potentials for the various forms of polyaniline. Where possible, comparison is made to experiment, with very favorable results. The discussion emphasizes the electrochemistry of polyaniline in aqueous media and the structural evolution of the polymer during electrochemical oxidation and reduction. A model is proposed for the redox behavior of polyaniline, which is consistent with experiment and VEH predictions.

Introduction

Polyaniline, known for over seventy years as the precursor to aniline black, has recently enjoyed a revival of scientific interest as a conducting polymer with good environmental stability and high potential as an electrode material in conducting polymer batteries [1, 2]. The redox chemistry of polyaniline is complicated by the myriad of possible chemical structures for the polymer backbone. This is especially true in aqueous media, where protonation and deprotonation of the nitrogen in the polymer backbone occur in concert with electrochemical oxidation and reduction [1, 2]. Polyaniline (PAN), referred to in the literature as the leuco base polymer, is an insulator with a large band gap.

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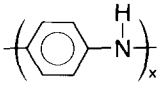
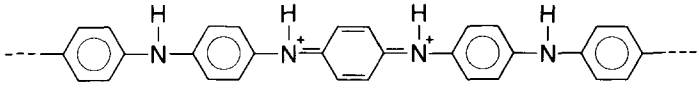


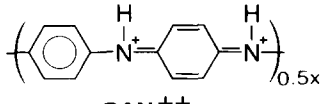
PAN

Oxidation of this material produces radical cations on the chains. This oxidation has also been described [1] as a two-electron process for yielding dications (or bipolarons) on the chains with the following (proposed) structure:



This doubly-charged defect with its quinoid linkage is analogous to the dication or bipolaron species identified spectroscopically in several aromatic-containing conducting polymer systems, including polyphenylene, polypyrrole and polythiophene [3]. In polyaniline, however, it is likely that the dication is more localized as shown above. This localization might, in fact, make the dication less stable with respect to break up into two radical cations, or polarons.

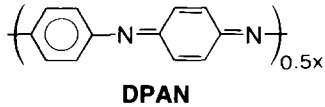
'Complete' oxidation would yield a polymer (PAN^{++}) of structure



PAN^{++}

As would also be expected with other conjugated polymers, on complete emptying of the highest occupied, π-electron band, PAN^{++} is expected to be an insulator. Experiments on PAN by Paul *et al.* [4] would seem to bear out this expectation. They observe that oxidation of PAN produces a conducting composition, which on further oxidation reverts to an insulating state. It has been suggested that the most conducting form of doped PAN has a degree of oxidation of about 0.5 [1, 2, 4].

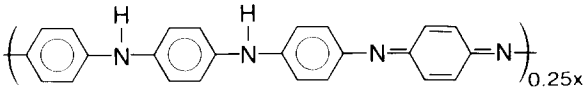
Removal of protons from PAN^{++} produces a neutral conjugated polymer, which we will refer to as dehydrogenated PAN or DPAN.



DPAN

This polymer, which has the same backbone structure as the eight-unit oligomer pernigraniline, is unique among known conjugated polymers in that the quinoid structure of the backbone is preserved after removal of the charge. This behaviour is directly responsible for the observed facile and reversible protonic doping of these polymers. DPAN can be produced, in

principle, by exposing fully oxidized PAN (PAN^{++}) to a base that extracts the protons to yield DPAN. If oxidation is not complete, the procedure would be expected to yield a polymer with the number of DPAN linkages corresponding to the degree of oxidation of the PAN starting material. For example, if the oxidation of PAN is carried out only to half completion ($PAN^{+0.5}$), treatment with base will yield an emeraldine base structure, which we will refer to as polyemeraldine (PEM):



PEM

(PEM can be thought of as being half-way between PAN and DPAN, just as emeraldine is half-way between leucoemeraldine and pernigraniline.) It is uncertain whether or not DPAN has been authentically prepared or if the products are intermediate structures such as PEM. In any case, the resulting polymer has a significantly lower band gap (about 1.4 eV) than the parent compound, PAN.

All of the above materials have been discussed as playing an important role in the electrochemistry of polyaniline. In this paper, we calculate geometries and electronic structures of various charged and uncharged forms of polyaniline. Our basic approach is summarized briefly in Section 2. Results of calculations are presented and discussed in Section 3.

2. Theoretical approach

We have had considerable success with the following general scheme [5, 6]. The MNDO (Modified Neglect of Differential Overlap) semiempirical theoretical method [7] is used to calculate the atomic geometries of oligomers of PAN, PAN^{++}, DPAN and PEM. Predicted geometries extracted from the central portion of the oligomer are taken as defining a unit cell, which is then used as input to the Valence Effective Hamiltonian (VEH) scheme [8, 9] to calculate the band structure of the polymer and predict various electronic properties, including electrochemical redox potentials [5]. MNDO has a well-documented history of accurate geometry predictions [7]; VEH has a very successful track record for accurately predicting electronic and electrochemical properties of conjugated molecules and polymers [5, 9 - 13]. Each of these methods is briefly discussed in the remainder of this Section.

MNDO, developed by Dewar and Thiel [7], is a method that has been widely applied to organic molecules with good success in predicting ground-state properties, especially geometries. Its results are self-consistent field solutions to the Hartree–Fock Hamiltonian including all s and p valence electrons. MNDO computational feasibility for large molecular systems comes

from neglecting certain selected sets of multicenter integrals and parameterizing some of the remaining ones to optimize the predictive capabilities of the scheme for molecular geometries and heats of formation.

The Valence Effective Hamiltonian (VEH) technique is based on a methodology for obtaining molecular one-electron Hamiltonians from first principles originally devised by Nicolas and Durand [8]. An effective Fock operator is derived from Hartree–Fock *ab initio* double-zeta quality results on small molecules and transferred to larger systems. The VEH method produces one-electron energies (or band structures) of double-zeta quality with a computational cost comparable to that of the Extended Hückel technique. The VEH technique is completely theoretical and avoids SCF iterative cycles. No information pertaining to the excited states is included in the effective Fock operator. As a result, no special attention should, in principle, be given to the unoccupied levels. However, for conjugated polymeric systems [5, 9 - 13], very good agreement between experiment and theory has been obtained for the lowest optical energy transition; an explanation for this surprisingly good agreement has only recently been given [14].

3. Results and discussion

3.1. Molecular geometries

We have studied oligomers of PAN, PAN^{++} and DPAN using the MNDO technique. In order to extract unit cell coordinate data for subsequent electronic band-structure calculations, the length of the oligomers is always taken at least two ring units longer than the unit cell of the polymer for which it serves as a model; this is to avoid end effect. Geometry optimizations are performed using a center of symmetry at the middle of the oligomer.

For PAN, all of the rings are found to be predominantly benzenoid in character. All C—C bonds, however, are not exactly equal; those connecting the ortho and meta carbons are calculated to be 1.40 Å long, while the remaining four bonds are 1.42 Å long. A similar, slightly quinoid character is also found experimentally in poly(*p*-phenylene) oligomers [15]. When the hydrogens are removed (DPAN) or an equal number of electrons are removed (PAN^{++}), the rings alternate along the chain between being benzenoid (as above) and strongly quinoid; the quinoid rings have four bonds of length 1.46 Å and two of length 1.36 Å.

The torsion angle (the dihedral angle between the planes of adjacent rings) is difficult to calculate accurately because, at the MNDO level of approximation, there is not much energy associated with the torsion. Both PAN and PAN^{++} optimize with MNDO to 90° torsion angles and a C—N—C bond angle of 127°. DPAN optimizes to a torsion angle of 70°; however, this value is quite sensitive to the details of how the molecular topology and symmetry are specified to the MNDO program [16]. This is due to the softness of the MNDO force constant associated with the torsional motion of

adjacent rings; we find that the difference between a 90° twist and a 30° twist is only about 3 kcal/mole, in good agreement with other work [17]. It is likely that this torsion angle is strongly affected by crystal packing considerations. For example, in poly(*p*-phenylene) oligomers, the torsion angle is measured to be about 42° in the gas phase [18] and only 23° in the solid state [15, 19]. Thus we might expect the torsion angle in all of the PAN materials to be closer to planar than to the predictions for isolated molecules. Crystal structures of short oligomers (diphenylamines) have been studied experimentally [20 - 22]; the measured torsion angles lie in the range 23 - 65°, depending on the termination group and its charge. These values are considerably lower than those predicted from MNDO calculations on the isolated molecules.

3.2. Electronic and electrochemical properties

VEH calculations have been carried out for PAN, DPAN and PAN^{++} with three different choices for the torsion angle between adjacent phenyl rings: (a) a large angle corresponding to the minimum energy configuration given by MNDO; (b) a 30° torsion angle, chosen as the minimum angle consistent with an acceptable degree of steric interaction between hydrogen atoms on adjacent rings; and (c) a 0° torsion angle achieved for polymer chains where adjacent rings are bridged with $-CH_2-$ linkages. For the latter two, the geometry is otherwise fully optimized with MNDO. Preliminary calculations on PAN and DPAN, using unoptimized geometries, have been reported by Thémans *et al.* [23]. A more detailed discussion of the evolution of the electronic properties of DPAN as a function of torsion angle is given in ref. 17.

VEH band structures for PAN, DPAN and PAN^{++} are shown in Fig. 1 for a torsion angle of 30°. The unit cell in each case is chosen to contain two nitrogens and two rings. Table 1 gives a summary of the principal VEH

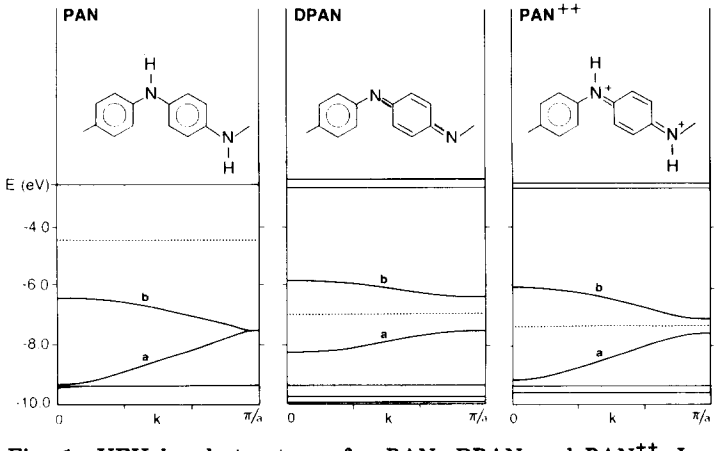


Fig. 1. VEH band structures for PAN, DPAN and PAN^{++}. In each case unit cells are chosen to contain two rings and two nitrogens, as shown in the illustrations. The Fermi level, which divides occupied and unoccupied levels, is shown by the dashed line.

TABLE 1

VEH predictions for the electronic and electrochemical properties of various forms of polyaniline

Polymer[a]	Ionization potential (V)	Band gap (eV)	Band width (eV)	Oxidation potential (V *vs.* SCE)	Reduction potential (V *vs.* SCE)
PAN (90°)	5.2	~4.5	2.1	+0.8	~−3.7
PAN (30°)	4.4	3.8	3.0	+0.0	−3.8
PAN (0°)	4.2	3.6	3.0	−0.2	−3.8
DPAN (90°)	6.1	2.1	0.0	+1.7	−0.4
DPAN (30°)	5.6	1.2	0.7	+1.2	−0.1
DPAN (0°)	5.3	0.7	1.5	+0.9	+0.2
PAN^{++} (90°)	6.1	0.6	1.1	+1.7	+1.1
PAN^{++} (30°)	5.6	0.5	1.6	+1.2	+0.7
PAN^{++} (0°)	5.4	0.3	2.0	+1.0	+0.7

[a]Number in parentheses is the torsion angle (dihedral angle between adjacent rings on the chain).

results of all three angles. The two highest occupied bands for PAN (labeled a and b in Fig. 1) have considerable dispersion and a fairly large total bandwidth (3.0 eV). (Note that if the full, glide-plane symmetry of PAN were used in the calculation, the band structure would unfold so that a and b become a single band.) Bands a and b are composed of delocalized π orbitals from the rings with a strong admixture of nitrogen p_z orbitals. Deprotonation of PAN to produce DPAN corresponds to a complete removal of electrons from band a in PAN. When the geometry is allowed to relax, the glide-plane symmetry is lifted. As a result, bands a and b are no longer degenerate at the band edge (π/a), so that a gap develops between band a (now unoccupied) and band b (the new highest occupied band), as shown in the middle panel of Fig. 1. Oxidation of PAN (removal of two electrons per repeat unit) yields PAN^{++}, whose band structure is given in the right panel of Fig. 1. This oxidation also corresponds to the emptying of band a of PAN and the resulting band structure is very similar to that of DPAN.

Ionization potentials, band gaps and bandwidths derived from the VEH band structures are presented in Table 1. The ionization potentials (IP) quoted in the Table have been corrected from gas phase to solid state values by subtracting 1.9 eV as a polarization energy correction [9 - 12]. The ionization potential of PAN predicted by VEH theory varies from 4.2 to 5.2 eV depending on the torsion angle. Though we believe the 30° torsion angle results to be the most appropriate for comparison to experiment, this must be recognized as a point of uncertainity at present. In order to make experimental comparisons, we assume here a 30° torsion angle for all three polymers. With that assumption, the IP for PAN is predicted to be at 4.4 eV, or about 0.3 eV less than that for polyacetylene and 1.1 eV less than that for poly(*p*-phenylene) [10]. We are not aware of any experimental measure-

ments of IP for PAN or DPAN. The band gap for PAN is predicted at about 3.8 eV, reasonably close to experiment (about 3.3 eV [24]). The bandwidth, which includes both bands a and b, is fairly large (3.0 eV), comparable to that for poly(*p*-phenylene) (3.5 eV) [10]. The IP for DPAN (5.6 eV) is predicted to be significantly higher than for PAN, though the band gap (1.2 eV) is predicted to be significantly lower. The VEH result for the band gap of DPAN is in good agreement with experiment (1.4 eV [25]). The band gap for PAN^{++} is predicted to be 0.5 eV, consistent with the experimental absorption spectra of oxidized PAN [24. 25]. We have also carried out VEH calculations for polyemeraldine (PEM); the results are very similar to those for DPAN.

We now turn to the discussion of electrochemical experiments in aqueous media [1]. The oxidation of PAN observed with cyclic voltammetry shows two waves: the first wave (Ox_1) has an onset at about 0.0 V and a peak at about 0.2 V and is insensitive to pH (above pH 0); the second wave (Ox_2) occurs in the range 0.2 - 0.8 V and is strongly pH dependent. (All quoted voltages are obtained in aqueous media with respect to an SCE reference.) At high pH values, the two waves are no longer well separated; a single peak at about 0.1 V could be expected if the pH dependence for Ox_2 is extrapolated to pH values outside the measured range. The first wave does show a pH dependence at very low pH values; however, since the amine nitrogens in PAN are probably being protonated in that range, we ignore this pH region for the present discussion. The second wave shows a pH dependence of 0.120 V per pH unit, suggesting the involvement of two protons per oxidation event. The reduction waves, Red_1 and Red_2, show qualitatively the same behavior: Red_2 occurs in the range 0.2 - 0.8 V, dependent on pH in the same manner as Ox_2; Red_1 occurs at about 0.1 V, independent of pH above pH = 0 [1]. (Our own work shows Ox_2 and Red_1 to be independent of pH only in the range 1.5 to 4.0).

Huang *et al.* [1] have given an interpretation of the cyclic voltammetry results, which is briefly summarized as follows. Ox_1 is attributed to the oxidation of PAN to produce dication species on the chains, eventually producing $PAN^{+0.5}$ at the end of the first wave. (They describe $PAN^{+0.5}$ as having a PEM structure with the imine nitrogens protonated.) The onset of this process would just be the oxidation of PAN,

$$PAN = PAN^{+\bullet} + 1e \qquad (1)$$

Since no hydrogen atoms are involved in this oxidation, no pH dependence is expected for reaction (1) and none is observed experimentally. Ox_2 is attributed to further oxidation to produce DPAN by the reaction

$$PAN^{+\bullet} = DPAN + 2H^+ + 1e \qquad (2)$$

Since the ratio of protons to electrons is two in this reaction, the pH dependence is expected from the Nernst equation to be 0.118 V per pH unit, in good agreement with experiment. Red_2 and Red_1 are simply the reverse of these processes.

Our theoretical results are consistent with this model. We predict reaction (1) to have an onset at 0.0 V, precisely the experimental value. (See PAN(30°) results in Table 1.) We have considered theoretically only the reverse of reaction (2) in the absence of pH effect, *i.e.*, the reduction of DPAN,

$$DPAN + 1e = DPAN^{-\bullet} \quad (3)$$

This reduction would be followed by the addition of two protons to yield $PAN^{+\bullet}$ in a pH-dependent process. At high pH values, where Red_1 and Red_2 occur at nearly the same voltage (~0.1 V), pH effects are minimum and the energetics of reaction (2) would closely approach those of the reverse of reaction (3). The VEH prediction for reaction (3) is −0.1 V, in reasonable agreement with experiment (0.1 V).

Though this model and our theoretical results are in good accord with experiment, we question the identification of DPAN as the final product of the oxidation process. It seems unlikely that DPAN would exist in its neutral form in highly acidic media. In other words, the equilibrium reaction

$$DPAN + 2H^+ = PAN^{++} \quad (4)$$

should be pushed toward PAN^{++} at high proton concentrations (the imine nitrogens of DPAN being protonated during the process). This is expected on the basis of the behavior of the emeraldine base in acidic media [2]. Indeed, an electrochemical study of the polyaniline oligomer, N, N′-dipheny/*p*-phenylenediamine, has demonstrated [26] its two-step oxidation to a radical cation and a dication in a strongly acidic solution ($>10^{-4}$ M $HClO_4$ in acetic acid). This reaction is equivalent in our case to

$$PANH^+ \longrightarrow PAN^{+\bullet} + H^+ + 1e \quad (5)$$

$$PAN^{+\bullet} \longrightarrow PAN^{++} + 1e \quad (6)$$

where $PANH^+$ is protonated PAN. Reaction (5) corresponds to Ox_1 in the low pH range (pH <0.0); reaction (6) corresponds to Ox_2. If PAN^{++} is the final product in the polymer electrochemistry, then Ox_2 would be interpreted as reaction (6). However, this reaction would show no pH dependence, in disagreement with experiment. This dilemma is resolved if we view reactions (2) and (6) to be in competition, so that the final product of the oxidation of PAN is dependent on pH in a manner which would be described by the equilibirum reaction (4). Thus at low pH, reaction (6) is active, and at high pH, reaction (2) predominates. Red_2 in highly acidic media (having an onset at about 0.8 V) could then be ascribed, at least partially, to reaction (6), which VEH theory predicts at 0.7 V. At high pH, the electrochemistry (and the interpretation with regard to VEH theory) would be the same as with the model of Huang *et al.* [1]. A prediction of our model would be the observation of the oxidation of DPAN in high pH or in non-aqueous media at about 1.2 V; this oxidation would not be observed in low pH media, since the concentration of DPAN would be low.

In summary, the VEH predictions for the electronic and electrochemical properties of various forms of polyaniline are in good agreement with available experiments. We have proposed an alternative model for the explanation of the oxidation and reduction of PAN, which is consistent with experiment and with the predictions of VEH theory.

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