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Theoretical investigation of the proton effect on electropolymerization of aniline

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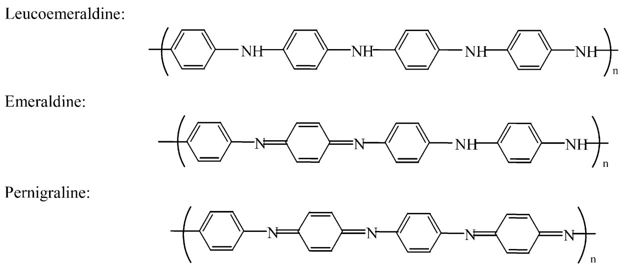
Abstract

The effect of the protonation on electropolymerization of aniline was elucidated theoretically. It was shown that the proton effects stabilities of *p*-aminodiphenylamine which is the primary species formed following electrooxidation in acidic media. The position of protonation is elucidated. Geometrical optimizations and calculated energies (strain and total energy and heat of formation) and proton affinity values predict that the *p*-aminodiphenylamine is preferably protonated on the amine nitrogen between the phenyl rings. It is concluded that the polymer backbone is relaxed and the strained structure is removed upon stepwise protonation during the growth of the polymer.

Keywords: Aniline; *p*-Aminodiphenylamine; Polyaniline

1. Introduction

Electroactive polymers such as polyaniline [1,2], polypyrole [3,4] and polythiophene [5,6] have been of particular interest because of their electrical conductivity, stability and redox properties. Among them, polyaniline occupies an important place due to its specific doping and conductivity characteristics. Polyaniline is produced through electrooxidation of aniline in acidic aqueous or non-aqueous media [7–11]. Experimentally, neutral polyaniline has three base forms [1]. They are: (i) the leucoemeraldine base, which represents the fully reduced form, (ii) the emeraldine base, which is the half-oxidized form, (iii) the pernigraline base, which corresponds to the totally oxidized form. Polyaniline exists in a highly conducting form, the emeraldine salt, which is obtained simply either by protonation of emeraldine base or by partial oxidation of leucoemeraldine base.



Polymer backbone contains only *p*-aminodiphenylamine type dimer. The other units such as azobenzene, benzidine, hydroxyazobenzene are not present in the structure of the polymer [12,13].

Although there are many theoretical studies concerning polyaniline [14–19] no detailed work on the effect of protonation on the stabilities of various species involved during the polymer growth has been reported. One of them was performed by Davila et al. and suggested that protonation causes an increase in the linearity of polymer chains [15].

In this work the effect of protonation on the stabilities of various species which might get involved in the polymerization mechanism is investigated theoretically. The position

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of protonation of various species which take part in the growth of the polymer is also elucidated.

2. Computational methods

Geometrical optimization of aniline, aniline dimmers, aniline tetramer and their protonated forms were carried out at the semi-empirical Austin Model 1 (AM1) [20] and Molecular Mechanic (MM2 and MM + [21,22]) methods. The calculations were performed using MOPAC (MM2) in the Chem3D and HYPERCHEM 6.0 (AM1, MM +) package programs and using a Pentium III 600 MHz computer. These methods are used to investigate some complex structures such as polymers [14–16]. In the calculations of the total energies (TE) and heats of formation (H_f), semi-empirical AM1 method was used. The bond angles, bond orders and bond lengths were calculated using Molecular Mechanic MM2 method. Molecular Mechanic MM + method was used for calculation of strain energies (SE). The interaction potential $\nu(R)$ describes both bonding and non-bonding interactions. The bonding interactions are usually formulated as strain energy that is zero at some ideal configuration of the atoms and describe how the energy increase as the ideal configuration is deformed. The strain energy is computed at the end of an MM + energy minimization.

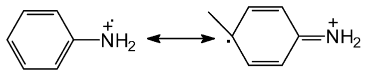
The proton affinity values were calculated from the computed heats of formation values for protonated and non-protonated species by utilizing the experimental heat of formation of the proton, 367.2 kcal/mol [23] according to the below formula (Eq. (1)).

$$\mathrm{PA} = 367.2 + \Delta H_f{}^{\circ}(\mathrm{B}) - \Delta H_f{}^{\circ}(\mathrm{BH}^+) \qquad (1)$$

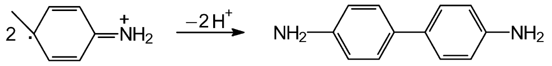
PA is proton affinity, $\Delta H_f{}^{\circ}(\mathrm{B})$ is heat of formation of B molecule, $\Delta H_f{}^{\circ}(\mathrm{BH}^+)$ is heat of formation of protonation form of B molecule.

3. Results and discussion

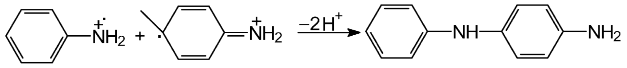
It is known from our earlier published results [11,24,25] that aniline is electrooxidized at a peak potential of +0.90 V vs. Ag/AgCl in acetonitrile/tetrabutylammonium perchlorate medium producing anilium cation radical. The addition of acid causes disappearance of this peak indicating protonation [24]. The protonated species gets oxidized at much higher potentials with a peak potential of +2.4 V vs. Ag/AgCl [24]. The protonated aniline gets reduced at −1.0 V vs. Ag/AgCl whereas, aniline itself shows no reduction peak in this medium up to −2.0 V Ag/AgCl [11]. Four different dimer formations are possible following the coupling of anilinium cation radicals. Hydroazobenzene and azobenzene formations are possible only in basic media [7,13] and will not be considered further. Benzidine and *p*-aminodiphenylamine are formed only in acidic media [12,13] as a result of the dimerization of anilinium cation radicals which gain extra stability in acidic media.



Anilinium cation radical



Benzidine



p-aminodiphenylamine

As seen from Table 1, while both of the non-delocalized dimers have considerably high strained energy values (14.34 and 14.28 kcal/mol), the Strain energies of their delocalized forms are comparatibly quite low (−2.87 and 2.36 kcal/mol) indicating that the delocalized forms of the dimers are more stable than their non-delocalized counterparts and the lone-pair electrons on nitrogen atoms in both dimers contribute to the conjugation with π-electrons in the adjacent phenyl rings. Furthermore, the comparison of total energy and heat of formation values (Table 1) of benzidine and *p*-aminodiphenylamine indicates that the formation of benzidine is favored.

Since the efficient polymer growth occurs in moderately acidic medium in acetonitrile the calculated values should be compared for protonated species as well. If the heats of formation and total energy values of monoprotonated species of these dimers are compared (Table 1) the formation of protonated benzidine is clearly preferred. When the strain energy values of the non-delocalized forms (9.55 and 1.97 kcal/mol) are compared, however, the order of priority is changed. The *p*-aminodiphenylamine protonated on the amino group between the two phenyl rings is now favored over the monoprotonated benzidine and *p*-aminodiphenylamine which is protonated on the terminal amino group. The SE of these three monoprotonated species are also calculated with delocalization taken into account. These values (−1.24 and 13.00 kcal/mol) indicate that protonated benzidine is more stable than *p*-aminodiphenylamine which is protonated on the amine nitrogen between the two phenyl rings. In other words the unavailability of the lone pair electrons on nitrogen upon protonation removes the conjugation possibility of the phenyl rings. Furthermore, the calculated proton affinity values of these three dimers indicate that *p*-aminodiphenylamine which is protonated on the amine nitrogen between the rings has the most basic character

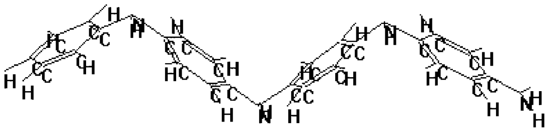
Table 1
Heats of formation, strain and TE for aniline dimers and their monoprotonated forms

	SE (kcal/mol)	SE (for delocalized species) (kcal/mol)	TE (kcal/mol)	H_f (kcal/mol)
$NH_2{-}C_6H_5{-}C_6H_5{-}NH_2$	14.34	−2.87	−48776.88	47.77
$C_6H_5{-}NH{-}C_6H_5{-}NH_2$	14.28	2.36	−48769.68	54.98
$NH_2{-}C_6H_5{-}C_6H_5{-}NH_3^+$	9.55	−1.24	−48943.09	196.47
$C_6H_5{-}NH_2^+{-}C_6H_5{-}NH_2$	1.97	13.00	−48937.75	202.30
$C_6H_5{-}NH{-}C_6H_5{-}NH_3^+$	13.53	9.98	−48930.25	209.31

(Table 2). The latter species has even greater proton affinity value than aniline itself as seen from the table. The proton affinity value of the aniline is given in literature as 211.4 kcal/mol [23].

Table 3 lists the C–N–C bond angles, C–N bond orders and C–N bond lengths of *p*-aminodiphenylamine and its protonated forms. The decrease in the bond order and bond angle and the increase in the bond length for the dimer which is protonated on the amine nitrogen between the rings give further evidence that the conjugation present between the nitrogen and the phenyl rings is removed as a result of protonation of this amino group.

Table 4 shows that increasing number of monomers in the oligomers of aniline causes a steady increase in the strain energy values. This means that aniline should not be polymerized in acetonitrile containing no proton. In acidic medium, on the other hand, the addition of each proton to aniline oligomers, for example tetramer, causes a steady decrease in the strain energy values (Table 5). It can thus be concluded that the polymer backbone is relaxed and strained structure, which is shown below, is removed upon stepwise protonation during the growth of the polymer. This structure was obtained from geometry optimization of tetramer.

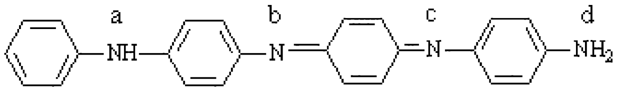


Furthermore, the protons are preferably added to the amino groups in the middle of the oligomers rather than to the end amino groups, which further facilitates the polymer growth. It was suggested by Ping and co-workers that more than 50% of the leucoemeraldine form could be protonated in strong acidic medium (pH < 1) [26].

Table 2
Proton affinity values of amine nitrogen (*) in aniline and its dimers

$C_6H_5{-}N^*H_2$	212.16
$NH_2{-}C_6H_5{-}C_6H_5{-}N^*H_2$	218.50
$C_6H_5{-}N^*H{-}C_6H_5{-}NH_2$	219.88
$C_6H_5{-}NH{-}C_6H_5{-}N^*H_2$	212.87

Partially oxidized form of polyaniline, emeraldine, contains both quinoid and benzenoid structures.



The proton affinity values of each nitrogen center in the emeraldine form of the tetramer were also calculated (Table 6). It is seen clearly that the proton affinity values of the monoprotonated emeraldine species which is protonated on the quinoid type nitrogen centers ((b) and (c)) are greater than that of the emeraldine protonated on the terminal nitrogen (d) or on the leucoemeraldine type nitrogen (a). This result provides a further evidence that protonation does not occur on the terminal nitrogen which would otherwise impede the polymer growth. The calculated C–N–C bond angles for protonated ($C{=}NH^+{-}C$) and non-protonated ($C{=}N{-}C$) emeraldine are 124.63 and 113.27°, respectively. This means that in emeraldine form, in contrast to the case of leucoemeraldine, the linearity of polymer backbone is increased upon protonation of imino nitrogen (N=) as proposed by Davila at et al. [15] and Boudreanx et al. [14].

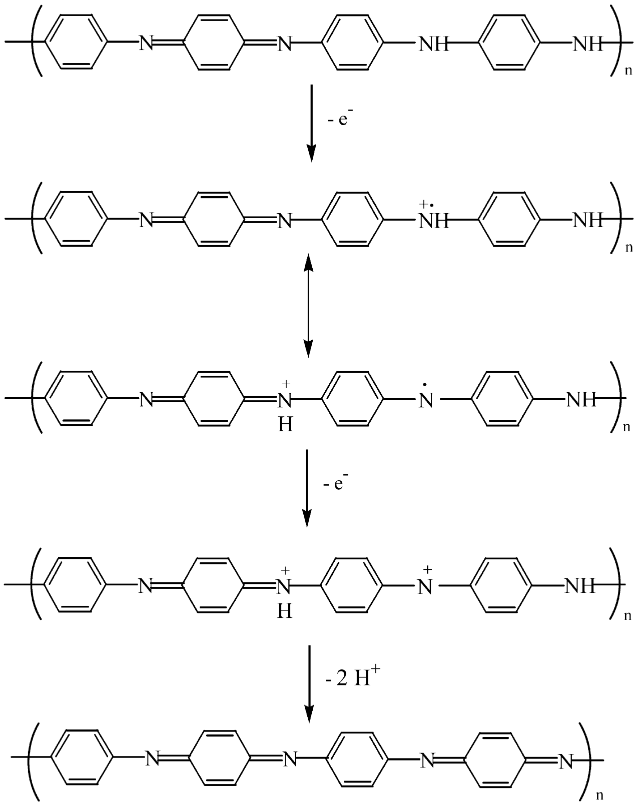
If no proton was present in the medium highly conducting polyemeraldine (2.76 S/cm) would be further oxidized to less conducting polypernigraline form (0.63 S/cm) as is the case in the acetonitrile observed experimentally [25].

Table 3
The measured $C{-}N^*{-}C$ bond angles, bond orders and bond lengths between the phenyl rings for *p*-aminodiphenylamine and its protonated species

	Bond order	Bond length (Å)	Bond angle (deg.)
$C_6H_5{-}N^*H{-}C_6H_5{-}NH_2$	1.340	1.434	137.6
$C_6H_5{-}N^*H_2^+{-}C_6H_5{-}NH_2$	1.000	1.452	111.5
$C_6H_5{-}N^*H{-}C_6H_5{-}NH_3^+$	1.326	1.412	137.7

Table 4
Strain and TE for aniline and its oligomers

	SE (kcal/mol)	TE (kcal/mol)
Aniline	4.27	−24705.92
Dimer (*p*-Aminodiphenylamine)	14.28	−48769.68
Trimer	32.12	−72832.47
Tetramer	46.75	−96894.88



Protonation of the quinoid type nitrogen centers in the moderately acidic medium also prevents the loss of NH proton from leucoemeraldine nitrogen to the quinoid N-centers, thus causing extra stability for the emeraldine.

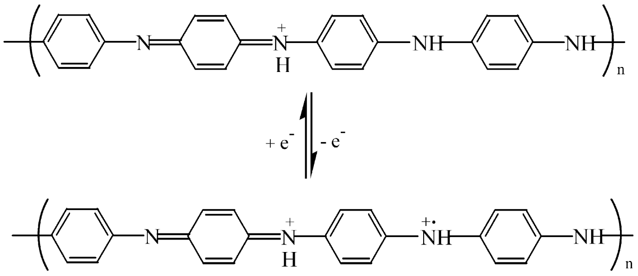


Table 5
Strain and TE for tetramer and its protonated species

	SE (kcal/mol)	TE (kcal/mol)
Tetramer	46.75	−96894.88
Tetramer + H^+	30.07	−97063.49
Tetramer + $2H^+$	15.72	−97169.01
Tetramer + $3H^+$	−2,57	−97229.84

Table 6
Proton affinity values of amine and imine nitrogen in emeraldine form of the tetramer

a	217.02
b	237.80
c	238.54
d	214.71

The presence of excess acid in the medium, however, in which polyaniline is growing also impedes the polymer growth as a result of the protonation of the end amino group as was observed experimentally [24]. The presence of moderate amounts of acids not only improves the stabilities of the aniline and *p*-aminodiphenylamine type cation radicals also causes the preferred protonation of these species which are primarily involved during the growth of highly conducting polyaniline [11].

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