Structural determination of a semiconductive tetramer of aniline by IR, UV-visible, ESR, XPS and mass spectroscopy techniques

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A tetramer of aniline was obtained by the chemical oxidation of aniline in sulphanilic acid. The analytical techniques of infrared, UV–visible and mass spectroscopy show formation of a relatively short conjugation length oligomer (tetraaniline). The electronic structure elucidated by X-ray photoelectron spectroscopy reveals that the tetraaniline skeleton contains both benzenoid, $[-NH-C_6H_4-NH-]$, and quinoid, $[-N=C_6H_4=N-]$, phenyl rings. In the oxidized state, the tetraaniline backbone containing alternate benzenoid and quinoid phenyl units structurally similar to emeraldine was not evident. Electron spin resonance and electrical conductivity data show localized charge carriers in the backbone. Experimental results predicting the molecular structure of tetraaniline are discussed.

1. Introduction

For the past decade, conducting organic polymers of polyacetylenes, polypyrrole, polythiophene, polyphenylenes, polymetallophthalocyanines, etc. have been a subject of considerable interest [1]. The potential applications of this new class of electronic materials have been anticipated in electronic industries. The highly conjugated carbon backbone of these organic polymers inherits unique electronic properties. In addition, the conjugated system also imparts environmental instability and insolubility to these materials which limits their practical applications. These two intriguing problems have stimulated further research interest in modifying existing conducting polymers to enhance their processability for fabricating electronic devices. Recently, a large number of efforts have been made particularly to synthesize new conducting polymers which are not only environmentally stable under ambient conditions but can be easily processed into ultrathin films [2–5]. Among these processable conducting polymers, polyanilines have attracted much attention. Polyaniline has a very simple organic structure. The base form of parent polyaniline can be depicted as below:
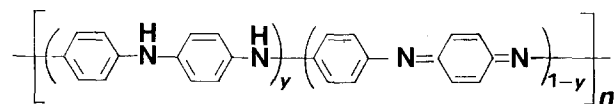
where y represents the degree of oxidation and the quinoid and benzenoid structures coexist in the polyaniline molecular chain.

Polyaniline has been known in the literature for almost 120 years under the name "aniline black". Letheby [6] and other researchers [7–12] synthesized the aniline compound by the anodic oxidation of aniline in acidic media. However, its importance as a conducting polymer has only been recently realized because of the unique electrochemical reduction and oxidation behaviour coupled with interesting electrophysical properties.

Polyaniline can be synthesized chemically as well as electrochemically to generate conductive thin films. Detailed studies on the synthesis, electrochemistry and physicochemical properties of polyanilines have been conducted by various research groups [13–20]. Polyaniline in the undoped state is an insulating material but its electrical conductivity reaches the metallic regime simply by doping ($\sigma = 10^{-10}$ to $10\,S\,cm^{-1}$). Therefore, polyaniline exhibits an insulator-to-metal transition [19]. MacDiarmid et al. [20] found that in polyaniline the counterions required for electroneutrality are protons, which clearly distinguishes it from other well-known conducting organic polymers. This conducting behaviour of polyaniline in conjunction with its peculiar redox electrochemistry led to a new class of electrode materials for applications in electrochemical batteries [21]. Polyaniline also exhibits multiple colour changes with the variation of electrical potential, and therefore it can find applications in electrochromic display devices [22].

From the practical point of view, polyaniline constitutes a blend of interesting properties including environmental stability, processability, redox chemistry, higher electrical conductivity, etc., which makes it a very valuable material for further studies. Although polyaniline has been extensively investigated from various aspects, it is still one of the most interesting organic polymers in order to develop structure–property relationships. The electrochemically synthesized polyaniline is insoluble, which restricts its solu-

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tion characterization and processability. On the other hand, polyaniline obtained via chemical oxidation of aniline in acidic media is a highly soluble and processable material. The chemical route also provides an avenue to understanding the basic chemistry involved in the polyaniline system by studying its oligomers as model compounds. In the present study, a tetramer of aniline was obtained by the chemical method, and its structural characterization by IR, UV, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) and mass spectroscopy techniques is reported in this communication.

2. Experimental procedure

Polyaniline can be synthesized by electrochemical as well as by chemical methods due to its ease of synthesis. In the present study, tetraaniline was obtained by a chemical route already reported in the literature by MacDiarmid et al. [23]. The analytical grade chemicals sulphanilic acid ($NH_2-C_6H_4-SO_3H$), ammonium persulphate [$(NH_4)_2S_2O_8$] and aniline ($C_6H_5-NH_2$) (Aldrich Chemical Co.) were used as received without any further purification. Chemical polymerization was accomplished by adding the aqueous solution of ammonium persulphate (oxidant) to an equimolar solution of aniline and sulphanilic acid (proton acid) at room temperature over a period of 30 min. A dark blue-black precipitate appeared immediately and the reaction mixture was kept overnight. The precipitate was filtered, washed with a copious amount of distilled water and dried under vacuum at 60 to 70 °C. The product is highly soluble in N,N-dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Thin-layer chromatography and mass spectroscopy reveal that the product contains various fractions. Intentionally, the low molecular weight fractions were carefully isolated. It is worth mentioning that tetramer was found to be one of the major fraction by weight. This product was further purified by dissolving in DMF and isolating the soluble fraction. Pure compound was obtained by the solvent extraction method under vacuum. A dark blue-green product in fine powdered form was obtained. Neutralization of the product was accomplished either with aqueous ammonia or ethanol–phenylhydrazine solution. The material also shows a pink colour with these reducing agents.

Various analytical techniques were employed for structural elucidation of the product. The molecular weight of the compound was determined by a mass spectrometer (Model VG 70SE, VG Analytical Instruments, UK) in DMSO. The FTIR spectra of oxidized as well as reduced polymer were recorded as a KBr pellet on an FTIR spectrophotometer (Alpha Centeuri, Mattson Instruments, Inc.). For recording the UV–visible spectra, a Shimadzu recording spectrophotometer UV-260 (Shimadzu, Japan) was used. UV–visible spectra were recorded in solution form by dissolving the sample powder in dimethyl formamide. For recording optical spectra in the solid state, the sample was dissolved in DMF and films were coated on a glass slide from solution. These films were

thoroughly dried under vacuum at room temperature to avoid solvent contamination. The ESR spectra of the powdered samples were recorded on an ESR spectrometer (IBM/Bruker ER-200 SRC) at room temperature. The g-value was calculated by comparing the sample with a reference of tetramethyl piperidine oxide (TEMPO) in mineral oil for which the g-value of 2.0062 is accurately known [24]. The XPS spectra of powder samples were recorded on an X-ray photoelectron spectrometer (Model 5100 ESCA system, Physical Electronics) using an $Mg_{K\alpha_{1,2}}$ (1245.9 eV) radiation source. The electrical conductivity was measured on the pressed pellets by a conventional two and/or four-probe method. The tetramer was doped with iodine in the vapour phase, while its solution doping was accomplished by treating the sample with 2 M hydrochloric acid for 6 to 8 h and then by subsequent washing and drying under vacuum.

3. Results and discussion
3.1. Mass spectroscopy

The product obtained by the chemical method is highly soluble in dimethylformamide and dimethylsulphoxide, like chemically prepared polymers of aniline. It seems that solubility, which is one of the most important factors from the solution characterization and processability viewpoints, has been tremendously enhanced. In contrast with electrochemically prepared polyanilines, chemically synthesized products are highly soluble and processable. When thin films of product coated on glass slides were viewed under the electron microscope, some needle-type crystal structure with pink-blue appearance was observed. In the present investigation, the product obtained via above-mentioned synthetic route has a molecular weight of 364 as determined by mass spectroscopy. This corresponds to an average number of four aniline units, [$C_{24}H_{20}N_4$]. The calculated molecular weight of a tetramer of aniline, [$C_{24}H_{22}N_4$], is 366; thus the determined molecular weight is lower than estimated but it fits well considering that two protons are released from the system during oxidation. Therefore the number of repeat units resulting from molecular weight determination indicates the interruption of the regular benzenoid sequence in the tetraaniline backbone.

If a chemical structure is derived for this tetraaniline, then molecular weight determination supports the existence of benzenoid and quinoid phenyl rings in the conjugated system similar to that of the emeraldine series. Viewed chemically, the tetraaniline system is composed of p-aminodiphenylamine and N-phenylquinonediimine structural units. In other words, tetraaniline contains amine and imine nitrogens in the backbone. This molecular weight is in good agreement with that predicted for an oxidized tetraaniline system. Since various molecular structures of tetraaniline are possible, the atomic sequence of the conjugated system will be discussed later after determining the exact chemical and electronic components from different analytical techniques.

3.2. Electrical conductivity

As-synthesized tetraaniline has an electrical conductivity of the order of $2.75 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$ due to contamination by the protonic acid. When the sample was neutralized with aqueous ammonia solution the electrical conductivity decreased only by an order of magnitude ($\sim 7.30 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$), unlike the behaviour most often seen in other conjugated organic polymers. Although the conductivity of the neutralized sample matches the emeraldine series, it is unlikely to be the conductivity of the insulating state. Since it was rather difficult to obtain tetraaniline in the insulating state by aqueous ammonia treatment, samples were therefore undoped by a vacuum pyrolysis technique as employed for polypyrrole by Ritsko et al. [25]. This thermal treatment produced no significant chemical changes (i.e. degradation) in tetraaniline, except that abstraction of counterions leads to a completely undoped state. When tetraaniline samples, both oxidized as well as reduced, were pyrolysed for a prolonged period under vacuum, an abrupt change in electrical conductivity was observed (Fig. 1). The electrical conductivity of neutralized and oxidized tetramers decreases to $\sim 4.42 \times 10^{-13}$ and $3.67 \times 10^{-11}\,\mathrm{S\,cm^{-1}}$, respectively, at 200 °C in a period of 5 to 6 days; thus semiconductive tetraanilines become insulators. These insulating tetraanilines are very sensitive to air, since the conductivity also changes rapidly by switching the samples between an inert and an oxygenated atmosphere.

Thus pristine material is an insulator, and the higher conductivity recorded for the directly synthesized sample just after oligomerization is associated with the oxidation. It may be that treatment with $\mathrm{NH_4OH}$ as well as with phenylhydrazine partially neutralizes the sample. When these pyrolysed samples were again redoped, either with iodine or 2 M HCl solution, their electrical conductivity increased by several order of magnitudes; with iodine doping the conductivity reached $\sim 4.8 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$, while HCl doping could raise it to $\sim 2.95 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$, similar to that of the as-synthesized sample. Similarly, the conductivity of the neutralized sample increased from $\sim 10^{-13}$ to $1.47 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ on iodine doping. The IR spectra recorded for the pyrolysed samples show the absence of $\mathrm{SO_3H}$ groups in the tetramer, indicating that contamination with the protonic acid

increases the electrical conductivity. Li et al. [26] synthesized soluble polyaniline by a similar chemical method, and the low molecular weight product (degree of polymerization = 11) obtained just after the synthesis showed an electrical conductivity of the order of $\sim 0.1\,\mathrm{S\,cm^{-1}}$. In an another study, Cao et al. [27] reported that the electrical conductivity of a series of aniline oligomers increases with the increase of conjugation length. If a comparison is made, then the electrical conductivity of this tetraaniline is in good agreement. However, a perfect relationship is not yet established but the lower conductivity results from the smaller conjugation length due to the restricted delocalization of charge carriers.

3.3. Infrared spectroscopy

Fig. 2 shows the IR spectra of tetraanilines. The various IR absorption bands observed were at 570, 688, 836, 1009, 1034, 1122, 1158, 1245, 1291, 1318, 1400, 1500, 1506, 1600, 1649, 2962, 3240 and $3450\,\mathrm{cm^{-1}}$. The present IR data were compared with those for a variety of aniline compounds [15, 27–29]. The absorption bands at 1245 and $1291\,\mathrm{cm^{-1}}$ are believed to be due to C–N vibrations, the C=N vibration band appears at $1600\,\mathrm{cm^{-1}}$. The $1649\,\mathrm{cm^{-1}}$ absorption band is associated with the C–C vibration mode. The characteristics of benzenoid and quinoid phenyl rings have been evidenced by the absorption bands at 1500 and $1600\,\mathrm{cm^{-1}}$ respectively. For tetraaniline, the characteristic $\mathrm{NH_2}$ and NH absorption bands appear around 3450 and $3240\,\mathrm{cm^{-1}}$, respectively. The absorption band corresponding to =NH stretching vibration was not visible [15, 27]. The presence of the C=N vibration mode indicates that benzenoid to quinoid changes take place in oxidized tetraaniline. The possible molecular structure of tetraaniline in oxidized and reduced states will be discussed later. The absorption band due to the C–H stretching appears at $2962\,\mathrm{cm^{-1}}$. Ohsaka et al. [29] studied the IR spectra of electrochemically synthesized polyaniline and reported that C–N bands show peaks around 1300 to 1310 and 1245 to $1250\,\mathrm{cm^{-1}}$, with a C=N band at 1600 to $1620\,\mathrm{cm^{-1}}$. The $-\mathrm{SO_3H}$ absorption band appears at $1400\,\mathrm{cm^{-1}}$, which indicates the presence of traces of $\mathrm{SO_3H}$ in the tetramer. When the samples were pyrolysed at 200 °C under vacuum for 7 days the elimination of protonic acid takes place
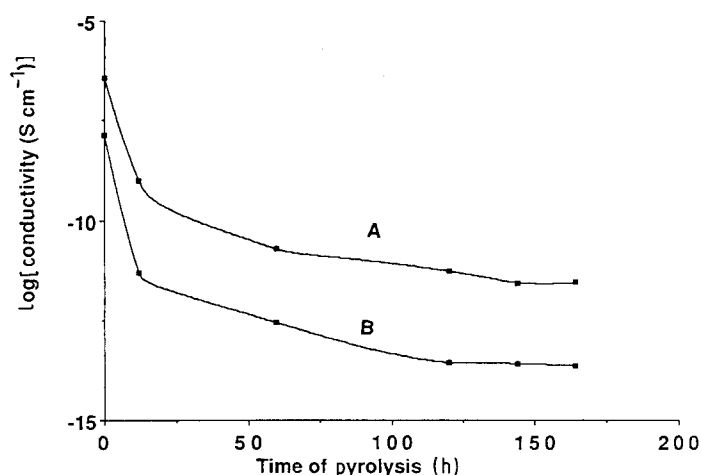

Figure 1 Variation of electrical conductivity as a function of pyrolysis time for (A) an oxidized tetraaniline sample and (B) a tetraaniline sample already neutralized with aqueous ammonia solution.
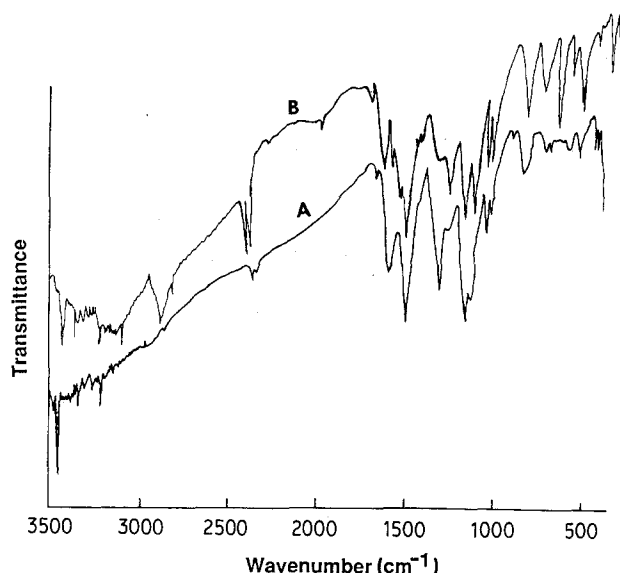
Figure 2 IR spectra of (A) an oxidized sample of tetraaniline and (B) after thermal treatment at 200 °C for 6 days under vacuum (reduced sample).

Figure 3 Optical absorption spectra of tetraaniline: (–––) in DMF solution, (–·–) coated film on glass slide, (· · ·) in DMF solution after adding a small amount of sulphanilic acid, (———) after treating the sample with aqueous ammonia solution, and (–···–) coated film on glass slide after adding sulphanilic acid.

and the absorption peak associated with the $-SO_3H$ group disappears.

Noticeable changes in the chemical components after thermal treatment are visible from the IR spectral data. For tetraaniline, IR absorption bands are slightly shifted in comparison with polyaniline, due to the structural differences. Furthermore, mostly electrochemically prepared polyanilines contain a mixture of oligomers, so the characteristic difference in IR spectral data from the chemically obtained sample is accounted for. In the present study, tetraaniline is a well-defined material unlike the anilines of different chain-length, so a slight shift in frequency and sharp absorption bands can be anticipated.

3.4. Optical absorption spectroscopy

Fig. 3 represents the electronic absorption spectra of tetraaniline in dimethylformamide solution as well as of the coated film on a glass slide. The optical absorption spectrum taken in DMF solution shows optical absorption bands at 370 and 555 nm. Neutralization with aqueous ammonia gives a pink colour, and a new absorption peak appears at 250 nm while the other two peaks shift to 355 and 540 nm. When a very small quantity of sulphanilic acid was added to the tetraaniline, a noticeable change in optical spectra was observed between the solution and solid-state conditions, probably due to the intermolecular interaction. The position of the electronic band at 295 nm is shifted to 310 nm in the case of a coated film, and the other two bands appear at 430 and 580 nm. Also in the solid-state spectrum, an additional band at 810 nm develops with the addition of sulphanilic acid which is not visible in the optical spectrum recorded in DMF solution.

Therefore depending upon the treatment of the sample, strong electronic band changes were observed. The optical band between 295 to 329 nm is associated with the π–π^* transition. For a variety of aniline
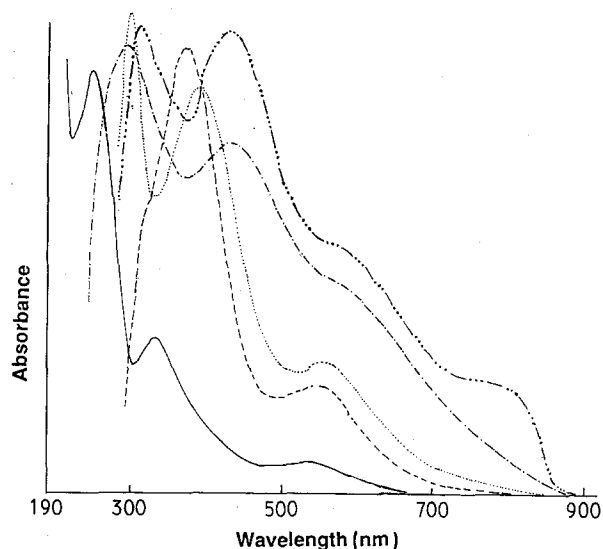
compounds, the π–π^* transition band appears between 285 and 325 nm and is strongly influenced by the conjugation length [27]. Only in DMF solution is the π–π^* transition band of tetraaniline not clearly visible. The optical band recorded at about 580 nm for the coated films shifts to 555 nm in DMF solution, which is associated with the existence of benzenoid and quinoid phenyl rings. Similarly a remarkable change in optical spectra at about 430 nm was noticed; this peak shifts to the higher-energy side, i.e. 390 nm in DMF solution. Cao et al. [27] suggested this peak position as a mid-gap absorption band in polyaniline.

Focke and Wnek [30] also reported the optical properties of various oligomeric products of aniline. Similar to the present results, a change in the optical spectra was observed for oligomers and polyaniline with an additional amount of appropriate proton acids. Lu et al. [31] studied the optical properties of polyaniline and optical bands at 320 and 525 nm were reported. Furthermore, the optical properties of polyanilines are affected by the redox behaviour. The optical bands shift to the higher-energy side as the average conjugation length of the aniline system increases. For example, the optical band at 395 nm in a phenyl-capped dimer shifts to 444 nm in the tetramer due to the extended π-electron conjugation [30]. A noticeable change in the optical spectra in solution and the solid state probably results from the degree of molecular interaction. The optical spectra in the present study show a short conjugation length, possessing benzenoid and quinoid phenyl rings in the oxidized state and only benzenoid structure in the reduced form. These results are consistent with the earlier studies of aniline compounds.

3.5. Electron spin resonance

The ESR spectrum of oxidized tetraaniline recorded at room temperature is shown in Fig. 4. The ESR spectra
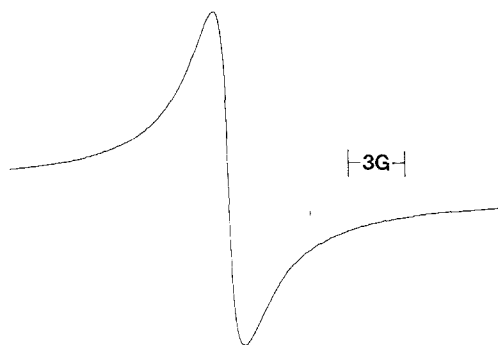
Figure 4 ESR spectrum of oxidized tetraaniline recorded at room temperature.

of both oxidized and reduced samples were symmetrical with a Gaussian line shape. A peak-to-peak linewidth (ΔH_{pp}) of 2.31 and 11.8 G were calculated for oxidized and reduced samples, respectively. The g-values of oxidized and reduced samples were found to be 2.0052 and 2.0033, respectively. Lu *et al.* [31] reported a g-value of 2.0036 for a highly conducting model compound of polyaniline. Glarum and Marshall [32] studied the *in situ* potential dependence of ESR in polyaniline and suggested that electrical conductivity and paramagnetism are correlated. For tetraaniline, the g-value and linewidth of the oxidized and reduced samples are similar to the previously reported ESR results [33, 34].

In a variety of conjugated organic polymers an exceptionally narrow linewidth indicates highly mobile charged defects in the polymer backbone. However, the oxidized tetraaniline consists of benzenoid [$-NH-C_6H_4-NH-$] and quinoid [$-N=C_6H_4=N-$] units in the backbone but the mobility of charged defects is localized due to the short conjugation length. The quinoid phenyl ring converts to a benzenoid unit after reduction, which further restricts the mobility of charged defects in the chain. This explains the broad ΔH_{pp} observed for the reduced sample. The ESR results show that the mobility of charged defects in tetraaniline is associated with the short conjugation length and depends upon the structural changes. Oxidized tetraaniline seems quite stable in an oxygenated atmosphere. No significant change in ESR spectra was observed after several days of exposure to air, which indicates good stability.

3.6. Photoelectron spectroscopy

X-ray photoelectron spectroscopy was employed to study the electronic structure of the tetraaniline. The XPS spectra show the presence of C1s, N1s, O1s and S2p atoms in oxidized tetraaniline. The C1s, N1s, S2p and O1s binding energy spectra of tetraaniline are shown in Fig. 5. The C1s spectrum consists of a broad peak at 285.45 eV with a full-width at half maximum (FWHM) of 1.59 eV, and another smaller peak at 286.84 eV (FWHM = 2.00 eV). The C1s core level at
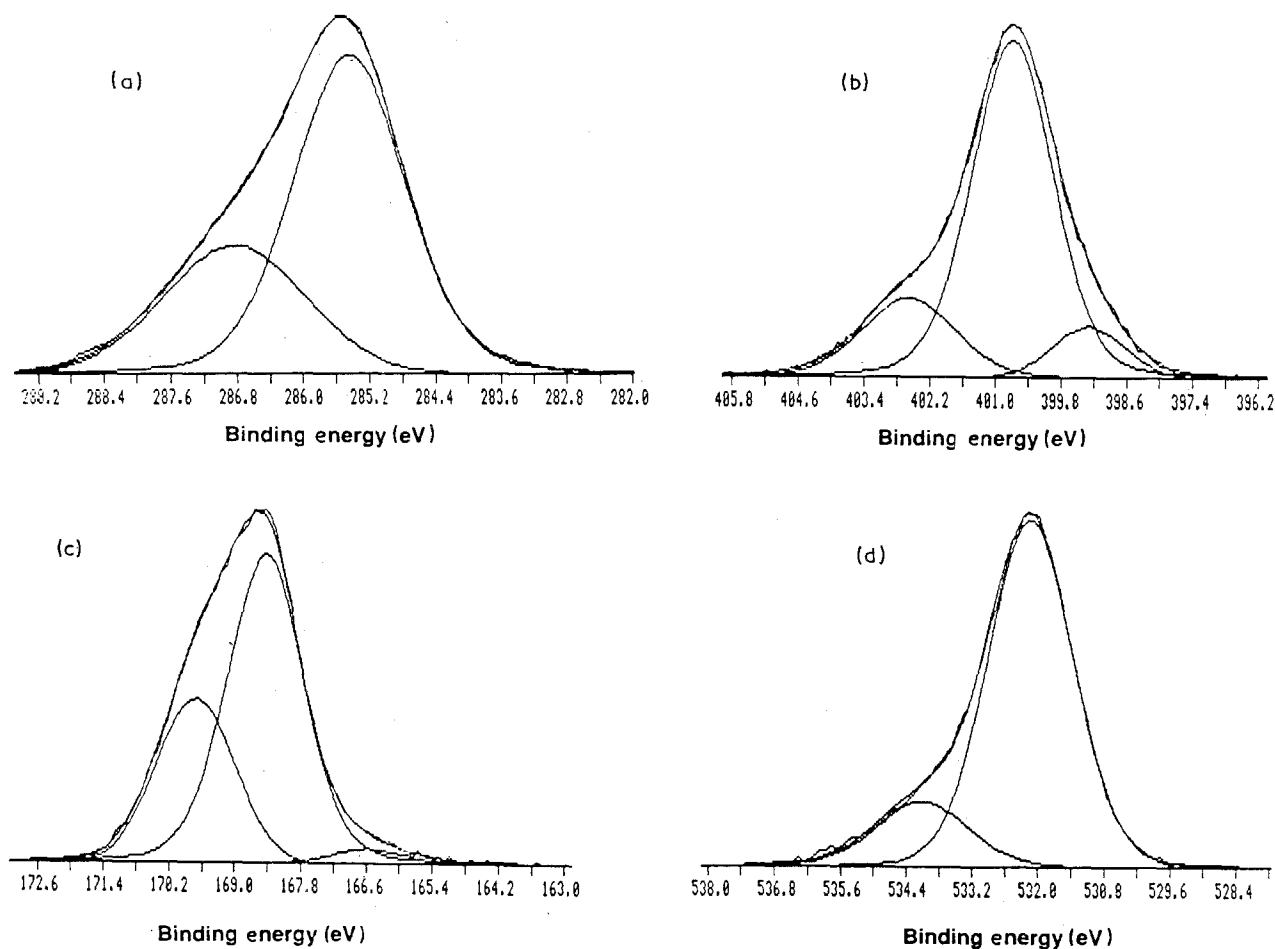

Figure 5 (a) C1s, (b) N1s, (c) S2p and (d) O1s binding energy spectra of oxidized tetraaniline obtained with an $Mg_{K\alpha_{1,2}}$ photon source.

285.45 eV displays the existence of quinoid structure in the compound, while a higher-energy peak evidences the benzenoid rings. The C1s binding energy is in good agreement with that reported by Snauwaert et al. [35] and Salaneck et al. [36] in a study of an electrochemically synthesized polyaniline (C1s = 285.50 eV).

The N1s spectra show one broad symmetrical peak at 400.70 eV with an FWHM of 1.75 eV. Also two other peaks appeared: a lower energy peak at 399.30 eV (FWHM = 1.57 eV), and a higher-energy peak at 402.59 eV (FWHM = 2.00 eV). Their splitting is 3.29 eV. The N1s peak at 399.30 eV evidences a quinoid phenyl structure, while benzenoid structure gives a peak at 402.59 eV; therefore in oxidized tetraaniline, quinoid and benzenoid structures exist in the carbon backbone and electronic charges reside on nitrogen atoms. Snauwaert et al. [35] reported a value of ~ 400.1 eV for N1s and suggested that the narrow N1s line reflects a well-defined structure of the polyaniline. The N1s core level at 400.70 eV supports a similar hypothesis. Therefore in the present case the observed shift of 3.29 eV towards higher binding energy shows that electronic changes do occur. A comparably lower binding energy in electrochemically prepared polyaniline is due to in situ doping.

The appearance of a chemical shift due to doping has been suggested in highly doped materials such as polypyrrole and graphite. The splitting of the N1s peak also indicates the different chemical nature of the nitrogen atom in the tetramer chain which is difficult to differentiate from other absorption spectra. Salaneck et al. [36] reported that electronic charges residing on nitrogen atoms are strongly influenced by protonation, so that a splitting is only visible for N1s spectra while carbon atoms remain unaffected by such a process. Interestingly enough, as with the IR absorption spectrum, the presence of an $-SO_3H$ group has been identified by the XPS technique. The S2p binding energy peaks appear at 168.47 (FWHM = 1.64 eV) and 169.73 eV (FWHM = 1.68 eV). The lower-energy peak resembles a para-phenylene type of bonding containing an $-SO_3H$ group at one end and an $-NH_2$ group at the para position of the aromatic ring ($-NH-C_6H_4-SO_3H$).
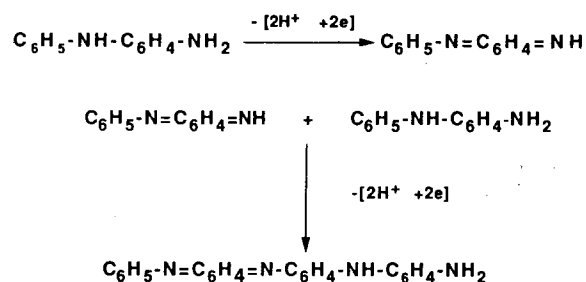
The higher-energy peak probably indicates an electronic adjustment to the $-SO_3H$ group of the tetraaniline backbone resulting from partial oxidation. Since the tetraaniline system consists of partially p-aminodiphenylamine and N-phenylquinonediimine molecular units, therefore phenyl repeat units are rather common, suggesting only the contribution of an $-SO_3H$ group. The O1s core levels appear at 532.16 eV (FWHM = 1.84 eV) and 534.14 eV (FWHM = 2.00 eV), showing the presence of two kinds of oxygen atom. The peak at 532.16 eV indicates the existence of SO_3H-type groups, while the higher-energy peak evidences the presence of water molecules which only come from the atmospheric moisture adsorbed to the surface of the sample (as commonly seen during XPS analysis).

Hayashi et al. [15] suggested that the oxidation of polyaniline results in electronic changes, i.e. benzenoid rings convert to quinonoid rings and subsequently a bipolaronic state appears which contribute in conduction mechanism. Similarly, MacDiarmid et al. [13] reported that the oxidation of polyaniline is entirely different to that of other conjugated polymers, and takes place through a protonation/deprotonation process which produces quinoid structure in the polyaniline backbone. A semiquinone-type structure of polyaniline on oxidation has been proposed by Cao et al. [27] and Epstein et al. [19]. The present XPS results evidence a tetraaniline skeleton possessing quinone structure in the oxidized state and residual charges centred on nitrogen atoms.

3.7. Molecular structure

Polyaniline differs from other highly conjugated polymers due to its complex redox chemistry. In polyaniline, electronic changes occurring in the polymer backbone are associated with the protonation and deprotonation of nitrogen atoms [37]. Emeraldine base is a perfect example of a model compound of oxidized forms of polyaniline, possessing equally reduced and oxidized repeat units in the conjugated system [38, 39]. The kinetics and reaction mechanism of the formation of the emeraldine series have been discussed in the literature [40–42]. Taking the case of tetraaniline, a similar free-radical mechanism could be operative; however, the reaction only goes half way. The schematic representation of the reaction process leading to the formation of tetraaniline written below is similar to that given by Green and Wolff [40] and Mohilner et al. [41]. The initial oxidation of aniline resulting in p-aminodiphenylamine has been described in detail by these authors. The initial oxidation steps being the same, formation of tetraaniline in an oxygenated atmosphere starting from an appropriate dimer can be expressed as follows:

$$C_6H_5\text{-}NH\text{-}C_6H_4\text{-}NH_2 \xrightarrow{-[2H^+ +2e]} C_6H_5\text{-}N=C_6H_4=NH$$

$$C_6H_5\text{-}N=C_6H_4=NH \quad + \quad C_6H_5\text{-}NH\text{-}C_6H_4\text{-}NH_2$$

$$\downarrow \scriptstyle -[2H^+ +2e]$$

$$C_6H_5\text{-}N=C_6H_4=N\text{-}C_6H_4\text{-}NH\text{-}C_6H_4\text{-}NH_2$$

The molecular weight determined by mass spectroscopy corresponds to the derived molecular structure of tetraaniline. The analytical techniques of IR, UV–visible and ESR used to elucidate the electronic and chemical structures of tetraaniline also suggest the existence of benzenoid and quinoid phenyl rings in the oligomer backbone. The interruption of the regular benzenoid phenyl ring sequence in oxidized tetraaniline, unlike the reduced form, has been supported by the XPS technique. The oxidation of tetraaniline which results from the release of two protons from reduced tetraaniline lead to a system composed of both benzenoid and quinoid phenyl rings which can be expressed by two possible molecular structures as shown in Fig. 6. One more possible resonance struc-
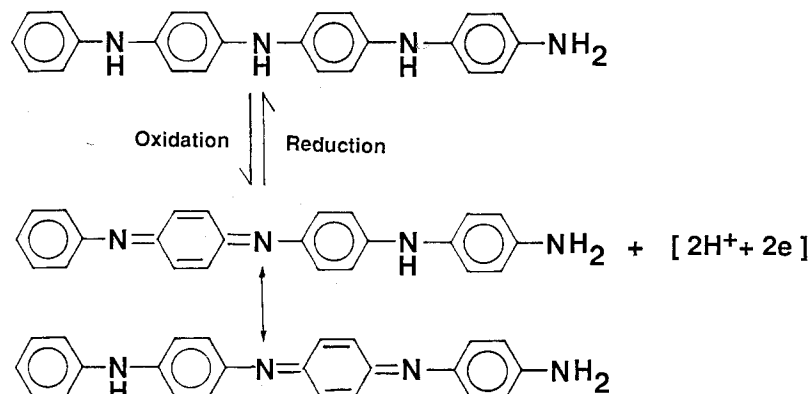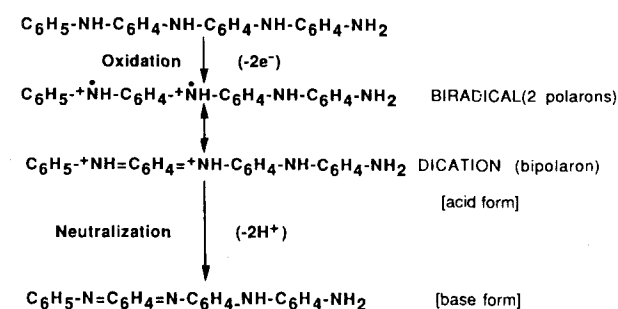
ture of oxidized tetraaniline can be derived from the following sequence:

$$C_6H_5-NH-C_6H_4-NH-C_6H_4-N=C_6H_4=NH$$
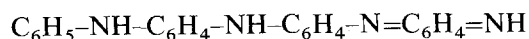
Although the IR spectral data show changes of benzenoid to quinoid phenyl rings during oxidation, as evidenced by the existence of a C=N absorption band at 1600 cm^{-1}, no =NH stretching vibrations were observed; therefore the possibility of a structure containing =NH bonding and an alternate sequence of benzenoid and quinoid phenyl rings in tetraaniline has to be excluded. Similarly, from optical absorption results, an intermolecular exciton band associated with such an alternative arrangement in tetraaniline was not observed by Conwell et al. [43]. These results are consistent with a tetramer of aniline as earlier reported in the literature [44, 45].

Other molecular structures of tetraaniline through radical cation formation on the backbone may also be proposed. The resonance structure of the oxidized state drawn above indicates greater stability of the system, while energetically a stable radical cation stage may not be feasible. Detailed cyclic voltammetric studies could predict the actual role of nitrogen and carbon atoms in connection with radical cations by shedding light on the redox chemistry of tetraaniline. From these results, tetraaniline can form a bridge between other oligomers of aniline in order to understand the basic chemistry of these model compounds and to develop a structure–property relationship.

The conduction mechanism in polyaniline has so far been explored by studying its oligomers, particularly the dimers and octamers. The formation of polarons and bipolarons on the short segments of tetraaniline can be shown to be similar to that of the emeraldine series. Oxidized tetraaniline is composed of both benzenoid and quinoid phenyl rings, and starting from the reduced form the different cationic states could be written with the following structure:

$$C_6H_5-NH-C_6H_4-NH-C_6H_4-NH-C_6H_4-NH_2$$

Oxidation ↓ (-2e⁻)

$$C_6H_5-\overset{\bullet}{N}H-C_6H_4-^+\overset{\bullet}{N}H-C_6H_4-NH-C_6H_4-NH_2$$ BIRADICAL(2 polarons)

$$C_6H_5-^+NH=C_6H_4=^+NH-C_6H_4-NH-C_6H_4-NH_2$$ DICATION (bipolaron)

[acid form]

Neutralization | (-2H⁺)

$$C_6H_5-N=C_6H_4=N-C_6H_4-NH-C_6H_4-NH_2$$ [base form]

Since both compounds differ structurally because of the conjugation length, therefore considering the mobility of charge carriers emeraldine is conducting while tetraaniline could not exceed the semiconductive regime even after complete oxidation. Because of the complicated redox chemistry, the conduction mechanism in polyaniline is not easily explainable. The formation of cations involves nitrogen atoms, so they are the main oxidation sites in the polyaniline backbone. The higher conductivity of emeraldine originates from the alternate arrangement of benzenoid and quinoid phenyl rings in the conjugated system, which seems infeasible in oxidized tetraaniline. An alternate arrangement similar to that of emeraldine may only be possible through cations, but from energetic considerations the resonance structure of oxidized tetraaniline proposed above may be more stable than any structure derived from radical cations.

Formation of cation structures may be a short-lived intermediate stage, but in a way their mobility contributes to conduction. The contribution of cations expressed by polarons and bipolarons in the transport mechanism of polyaniline has been interpreted by studying its model compounds [46–49]. Unlike polyheterocycles [50], in polyaniline polarons have been considered to be the charge carriers contributing to the transport process. Although dissociation of bipolarons into polarons may not be energetically favourable, experimental results on magnetic susceptibility, optical and transport properties support a bipolaron-to-polaron lattice transition [19, 39]. In the present study the ESR results indicate that charged defects are localized in tetraaniline which limit the magnitude of the electrical conductivity. The tetraaniline can be oxidized with protonic acids and noticeable changes in nitrogen and carbon atoms are evidenced by the spectroscopic studies. Oxidized tetraaniline is composed of benzenoid and quinoid phenyl rings but the transport behaviour depends upon their arrangement in the system; hence a more conducting material could be obtained if a well-defined conjugated system containing alternate benzenoid and quinoid phenyl rings was feasible. The electrophysical properties of the tetramer deviate from the phenyl-end-capped aniline tetramer [51, 52], due to structural differences. The present studies demonstrate that magnitude of transport properties is sensitive to the chemical structures.

Figure 6 The possible molecular structure of tetraaniline in reduced and oxidized states.

4. Conclusions

The comprehensive spectroscopic studies demonstrate the formation of a tetramer of aniline, consisting of benzenoid and quinoid phenyl rings in oxidized state. The electrical conductivity of oxidized tetramer does not increase beyond 4.8×10^{-5} S cm^{-1} probably due to the localized charge carriers.

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