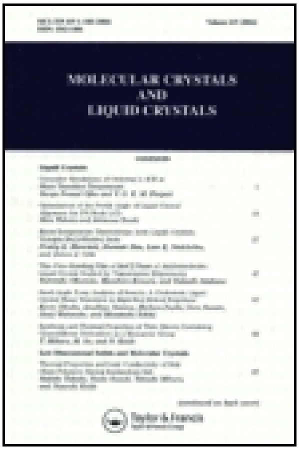

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Electrical and Optical Properties of Polyquinoxalines

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ELECTRICAL AND OPTICAL PROPERTIES OF POLYQUINOXALINES

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ABSTRACT We have synthesised a series of polyquinoxalines and model oligomers. This paper concentrates on optical and electrical properties of the five-ring dihydrotetra-azapentacene. When it is doped via electron and/or proton transfer, a variety of charged species are formed. Cyclic voltammetry reveals three oxidation states, discussed here in relation to conductivity data using HCl gas doping, optical absorption spectra, and preliminary ESR work.

INTRODUCTION

Ladder polymers have long been of interest because of their potential for high thermal stability and mechanical strength. If conjugated they necessarily have optimised π-overlap between neighbouring atoms on the chains, and potentially have strong orbital interaction between adjacent polymer chains. The polyquinoxalines (PQs) can be considered as analogues of polyaniline, and their study could be an important complement to work on the latter, which has been shown over the past few years to be a promising conducting material. Polyaniline itself is a highly conjugated system, with a rather high conductivity of ~10 Scm^{-1} in the emeraldine salt form, and it is very stable in air and water.

Recently, Dalton *et al*[1] have studied non-linear optical behaviour in certain polyquinoxalines, particularly those derivatised with vinylamine substituents, but little has been published on their electrical properties. We have previously reported preliminary work[2] on the synthesis of PQs and their "doping" by electron or proton transfer. A variety of charged species can be considered, in the context of their electronic transport processes; as for polyaniline, significant concentrations of polarons or bipolarons may be generated in the PQs by doping, and inter-chain proton hopping might significantly affect the bulk conductivity under strong doping conditions.

In parallel with our synthetic work on the ladder polymers, we have prepared a series of model quinoxaline oligomers (OQs) in order to examine the evolution of electronic properties in the series. We shall concentrate on a study of the OQs in this paper. It may be possible to use such oligomers in devices such as FETs, since they can be processed using high-vacuum evaporation techniques. Moreover, their electrochromism offers considerable potential for use as active components in colour displays.

Mobilities in conducting polymers would have to be enhanced considerably to match those in conventional FET devices. However, Xu *et al*[3] have shown that field effect mobilities in annealed oligothiophene films far exceed those in (amorphous) polythiophene: hence molecular organisation can be more important than high molecular weight.

EXPERIMENTAL

(Abbreviations for the oligomers studied in this work are: L3 for phenazine, L5 for dihydro(5,7,12,14-tetraazapentacene) and L7, L9 for the corresponding 7- and 9-ring analogues.)

Synthesis of PQ and OQs used polycondensations based on that proposed by Stille *et al*[4]; full details will appear elsewhere[5]. L3 was supplied by Aldrich. L5 was prepared by the method of Badger and Pettit[6] and by reaction of 2,5-dihydroxybenzoquinone (DHQ) with 1,2-diaminobenzene, either by fusion at 300C or in refluxing benzyl alcohol. L7 was prepared by thermal self-condensation of oxyaminophenazine (OAP) in an evacuated tube. L9 was synthesised from diaminophenazines (DAP) and DHQ, as for L5. Ladder PQs were prepared by Stille's method[4] at 160C or by self-condensing dichloro-diaminobenzenes.

Thin films of L5 were prepared by sublimation at ~10^{-5} Torr and 180C. L7 films were prepared by vacuum sublimation of OAP onto Al_2O_3 substrates with Pt electrodes for conductivity studies, then heated in inert gas to complete the reaction. PQ, L7 and L9 are not easily evaporated, so their 4-probe conductivities were measured on pressed pellets.

FTIR spectra were taken of thin films of L5 evaporated onto KBr discs. For UV/visible spectra, L5 was evaporated onto microscope slides and protonated by exposure to HCl fumes. Solution spectra of L5 were recorded in methanol. ^{1}H-nmr spectra were run on a Bruker 300 MHz spectrometer. For *in situ* UV-visible spectra, a thin cell consisting of (L5 on ITO glass)/ poly(acrylamido-methylpropanesulfonic acid gel)/(ITO glass) with an ITO quasi-reference electrode was used, controlled by a Thompson Autostat.

RESULTS AND DISCUSSION

Structural characterisation

Satisfactory chemical characterisation of the OQs was obtained by conventional analytical and spectroscopic techniques (described elsewhere). Only L3 and L5 were soluble enough for good solution-phase nmr spectra to be taken: solid-state nmr work is in progress.

While neutral L3 is the aromatic (fully-oxidised) phenazine, the other members of the series are hydrogenated at half the nitrogen centres. Our nmr data for L5 in DMSO-d_6 show a predominance of the asymmetric dihydro-form (I) suggested by Armand *et al*[7], rather than the centrosymmetric isomer (II) assumed by Badger and Pettit[6] and Jenekhe[8]; however the position of this tautomeric equilibrium is somewhat solvent-dependent. In any case, the OQs are quite strong bases; the imine nitrogens are readily protonated by dilute acids to give symmetrical and highly-coloured cations such as (III).

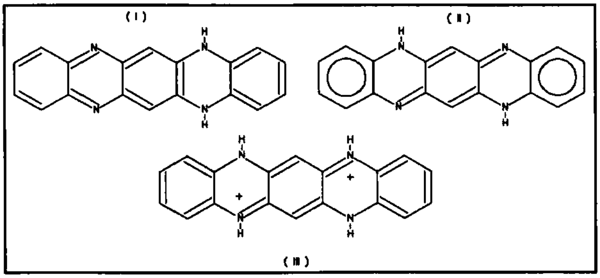

FIGURE 1 Forms of neutral and protonated L5

UV / Visible Spectroscopy

Basic calculations of the electronic states of several polycyclic azines have been made by Akimoto[9]. Simple Hückel theory was employed for the parent compounds, and a second order perturbation method was used to model the effects of meso-H atoms in the hydro-azines. The delocalisation energies and longest wavelength transitions for L5 isomers I and II were calculated to be very similar. The uv-visible spectrum of L5 in methanol (not shown) has two peaks at 550nm and 580 nm which belong to these isomers. DMSO has a higher relative permittivity and can stabilise the polar configuration (I).

Figure 2(A) shows the uv-visible spectrum of an evaporated thin film of L5 on a glass slide. The neutral (red) form has two main absorptions: a broad band centred at ~540 nm is the first π-π^* absorption with slight vibrational structure. The sharper band at 320 nm is the next higher π-π^* transition, with a weak shoulder attributable to non-bonding electrons being excited to an upper π^* band. The first n-π^* transition is probably obscured by the broad, low-energy $\pi\pi^*$ absorption. As protonation proceeds, the vibrational structure becomes more distinct, developing a series of sub-bands similar to those found in pentacene and some related azine compounds [Fig. 2(B)]. The intensities of the individual bands vary with protonation.

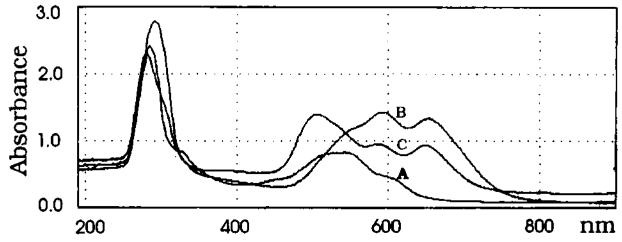

FIGURE 2 Optical absorption spectra of neutral and protonated L5

Selection rules governing these transitions change according to local symmetry variations of the molecular orbitals as the molecule becomes charged. Initial protonation turns the red L5 blue and it adopts structure III above. Under stronger acid conditions it turns mauve [Fig. 2(C)], when the extra protons become loosely bound and shared between the aza nitrogens. Such "hyperprotonation" becomes less favourable in solution, due to disruption of the hydrogen bonds, and the mauve state is then difficult to observe.

Cyclic voltammetry

This technique shows two redox couples, similarly to polyaniline (see Fig.3). One can draw classical molecular structures of L5 in various oxidation / protonation states which recall those of polyaniline, and accompanying these states there is a similar change of colour from blue to emerald green to yellow in acid solution. However, unlike polyaniline, L5 has no stable oxidised form, and requires chemical or electrochemical reduction to put it into its most conductive state.

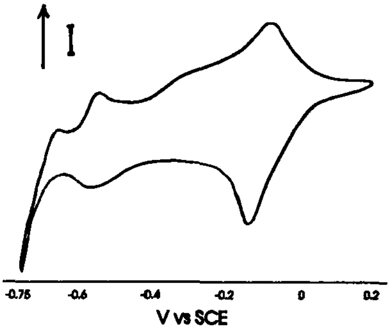

FIGURE 3 Cyclic voltammogram of L5 on ITO glass in 1M HCl electrolyte

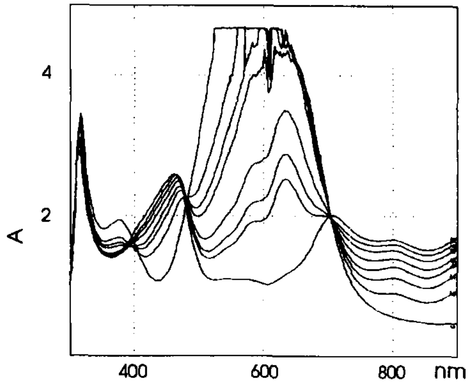

FIGURE 4 Optical spectra of ITO, L5/PolyAMPS/ITO cell vs potential.

In-situ UV-visible spectra of L5 vs. potential for a thin-film electrochemical cell are shown in Fig. 4. The salient features of the spectra as they evolve on reduction are the removal of the central peak at 600nm (with its vibrational structure), and the appearance of two new absorptions at 805 and about 950 nm. The formation of a radical cation [such as (V) in Fig. 5] is expected at this stage, and would be consistent with these new polaron-like transitions within the original HOMO-LUMO gap. On further reduction, the overall conjugation declines, and the fundamental π-π^* transitions increase in energy as the molecule becomes more benzenoid [structure (VI)]. The appearance of a new 450nm transition can be related to this.

(The lower sub-gap transitions are similarly expected to decline as the material is fully reduced. However, owing to attack of the ITO electrode at very negative potentials, complete reduction of the material was not achieved in this cell and some still remains in the conductive green state.)

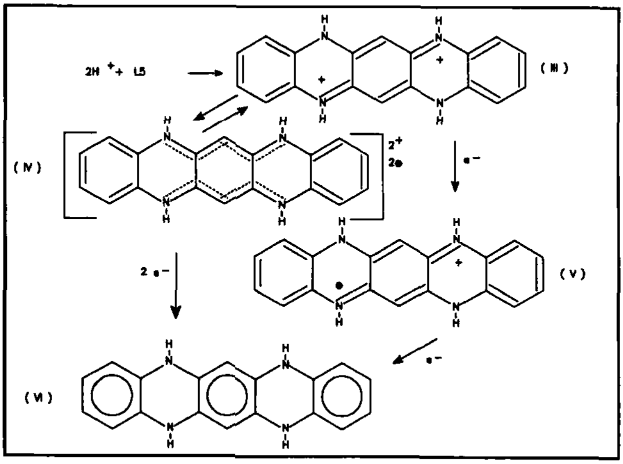

FIGURE 5 Protonation and redox equilibria for L5

The half-reduced (polaron) species (V) will have various canonical forms, all contributing to a significant unpaired spin concentration and possibly a higher conductivity. Indirect evidence for its higher conductivity is provided by the observation of much faster electrochemical switching from the green state to either yellow or blue (*cf.* emeraldine[10]), but *in situ* conductivity and ESR measurements are now under way to obtain more quantitative data.

Electrical Conductivity and ESR

It can be seen that there are two stages of protonation. Initially, the imine nitrogens are easily protonated, leading to the symmetrical molecule (III). However, the two extra charges may be pinned via Coulombic interaction with their counterions, rather than being fully delocalised. The conductivity at this stage remains quite low, with an activation energy of 0.78 eV. Further protonation results in "bridging" protons adhering symmetrically to the framework nitrogens. We propose that the electronic charge is then delocalised much more effectively, since a large rise in the bulk conductivity occurs [Fig. 6].

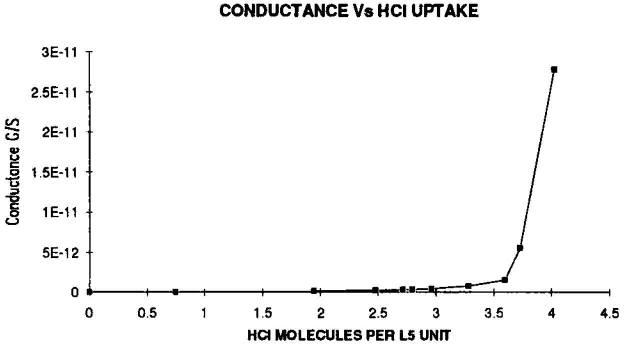

FIGURE 6 Conductance vs no. of HCl molecules absorbed per L5 unit

Preliminary ESR measurements on neutral L5 show only a broad singlet signal with partly-resolved hyperfine structure consistent with localised spin on the nitrogen sites. Protonation removes this absorption, producing a sharp delocalised spin signal. These spins partly disappear as the temperature is lowered to 77K, restoring some of the localised spin on the nitrogen sites. The mobile spin concentration is activated ($\Delta E=0.78$ eV), but the activation energy decreases drastically at the hyperprotonation stage.

We have now prepared chemically well-characterised OQ and PQ samples on which to make comparative physical measurements. Table 1 shows some conductivities of the polyquinoxaline series. As expected, the conductivity increases with the chain length. Upon protonic doping by exposure to HCl gas, the conductivities increase by a factor of 1000. However, we expect further large increases in conductivity in all these materials under conditions of strong protonation or electrochemical reduction, and this interesting prospect is being studied further.

TABLE 1: DOPED CONDUCTIVITIES AT AMBIENT TEMPERATURE

Compound	Undoped S m^{-1}	Doped S m^{-1}
L5 Film	$\sim 10^{-9}$	2×10^{-6}
L7 Film	$\sim 10^{-7}$	8×10^{-4}
L9 (Pellet)	$\sim 10^{-6}$	1.4×10^{-3}
Polymer	4.6×10^{-3}	0.16

CONCLUSION

The model oligomers and PQ polymers are currently under investigation; evaporable oligomer films of high purity are providing reproducible data for study of fundamental electronic properties. Protonic doping gives a conductive state, but significant further increases in conductivity and conduction electron spin signal occur both on "hyperprotonation" and on electrochemical reduction.

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REFERENCES

1. L. R. Dalton, Nat. Adv. Stu. Ins. Ser., Ser. E, **162**, 123 (1989)
2. P. Spearman, V. Montgomery and P.J.S. Foot, Paper G.IV.2, EMRS Fall Meeting, Strasbourg (1991)
3. B. Xu, D. Fichou, G. Horowitz and F. Garnier, Adv. Mater. **3**, 150 (1991)
4. J.K. Stille and E. Mainen, Polymer Lett. **4**, 39 (1966)
5. P. Spearman and P.J.S. Foot, in preparation
6. G.M. Badger and R. Pettit, J. Chem. Soc., 3211 (1951)
7. J. Armand, L. Boulares, C. Bellec and J. Pinson, Canad. J. Chem. **65**, 1619 (1987)
8. S.A. Jenekhe, Macromol. **24**, 1 (1991)
9. Y. Akimoto, Bull. Phys. Soc. Jpn. **29**, 460 (1956)
10. P.J.S. Foot and R. Simon, J. Phys. (D) **22**, 1598 (1989)