

SPECTROSCOPIC STUDY OF POLYAZOPYRROLES (A NARROW BAND GAP SYSTEM)

Jordan Del Nero, Bernardo Laks

Instituto de Física, Universidade Estadual de Campinas, 13083-970 Campinas, São Paulo, Brazil

Abstract

Polyazopyrroles are systems that are derived from the dipyrroles by inserting an azo group among the pyrroles rings. This new polymer present a significant decrease in energy gap lowering from 2.5 eV to 1.0 eV.

In this work we present a theoretical absorption spectrum obtained by the ZINDO/S method using the geometries optimized from the AM1 and PM3 semiempirical methods. As there are experimental evidences that this system presents polaron defects, we also include the effect of the polaron type defects on the electronic structure. The results are in good agreement with the experimental ones.

keywords: Polyazopyrrole, Polaron, Theoretical Absorption Spectrum.

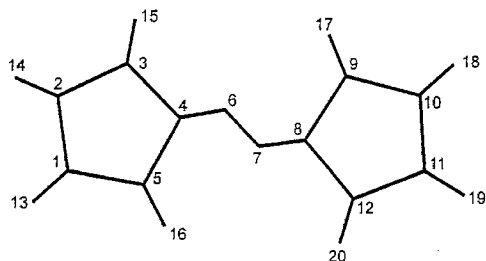
1. Introduction

Films of the Polyazopyrrole (PAzo) polymer was experimentally investigated through techniques of cyclic voltanometry (CV), UV-vis-NIR spectroscopy [1] with the objective of studying materials with high intrinsic conductivity. This High conductivity was obtained through the structural defects presence of polaron type.

Another material of the polyazopyrroles class is the polyazoarylenes that differ from PAzo by just possessing a pyrrole ring in the monomer and the polyazothiophenes substitution of the nitrogen atom of the rings for sulfur atoms.

In the figure 1 we can see esquematically the monomer structure for the polyazopyrrole, where the atoms 1 -> 4, 8, 10->12 are carbons and the atoms 5->7, 9 are nitrogens and 13->20 correspond to hydrogen.

Figure 1. PAzo monomer.



In this work we present the calculations of the electronic structure for the polyazopyrrole through semiempirical methods of AM1 and PM3 type. We treated the system with 1, 2 and 3 oligomeric units. These calculations were made using the MOPAC [2] program, including the molecules with +1,+2,-1,-2 charges.

The ZINDO/Spectroscopic [3] program was used to simulate the absorption spectrum coupled with the geometric structures obtained through AM1 and PM3, what allowed compatible

results with the experimental absorptions for these polymeric ones.

The method INDO/1 was chosen for being parametric specifically to describe the ultraviolet-visible optic transitions in organic materials.

For the calculations of optimization geometric and absorption we used a rigorous criterious for the convergence, when compared which original references [4], a step-size of 0.05 and the bond-orders matrix an approach of 10^{-5} , respectively for MOPAC and ZINDO.

2. Results and Discussion

In table 1 we can see the monomer charge distribution. The first column represents liquid charges in its respective site for the neutral molecule, that will be the comparison base for the charged systems.

Column 2 represents the modification by a positive charge on the whole molecule. When the sign of this "comparative charge" is positive that means the atom under the effect of the charge lose electron and it receive electron when the sign goes negative. In the columns 3,4 and 5 are striped the comparative charge, for respectively, N-(+2), N-(-1), N-(-2).

Analyzing columns 2 and 3 of table 1 show us a concentration of the charge in the nitrogens, mainly in N5 and N9 that correspond to the ring. The carbons C1, C3, C4, C10, C12, C8 exhibit an accentuated loss of charge. In the case of the charged systems negatively (columns 4 and 5) the comparative charge show us a charge gain in the carbons C1, C3, C10, C12 and in the nitrogen N6 and N7 with high concentration.

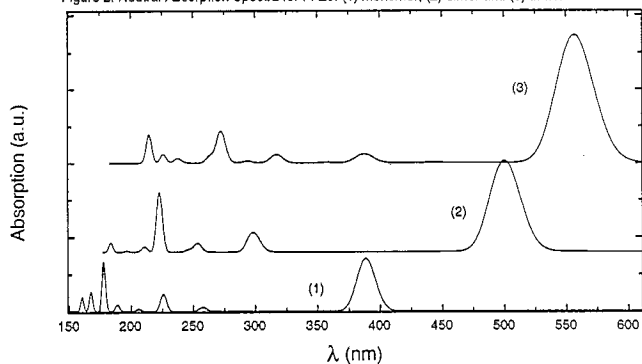
The absorption spectra of neutral polyazopyrrole can be seen in the figure 2 for the monomer, dimer and trimer, and the main absorptions correspond the transition H->L with the oscillator strenght of 1.0656, 1.8489, 2.5980, respectively.

Table 1. Liquid charges(column 1) and Comparative charge for monomer of PAzo.

C 1	-0.1076	-0.1605	-0.3219	0.1151	0.2439
C 2	-0.2140	-0.0191	-0.0514	-0.0277	-0.0718
C 3	-0.1180	-0.0836	-0.1220	0.1632	0.3290
C 4	-0.0772	-0.0809	-0.2002	-0.1180	-0.2250
N 5	-0.1666	0.0016	0.0214	0.0570	0.1301
N 6	-0.0581	0.0047	-0.0020	0.1635	0.2904
N 7	-0.0585	0.0049	-0.0019	0.1632	0.2900
C 8	-0.0772	-0.0811	-0.2003	-0.1181	-0.2249
N 9	-0.1667	0.0015	0.0213	0.0569	0.1304
C10	-0.1075	-0.1604	-0.3219	0.1152	0.2442
C11	-0.2139	-0.0189	-0.0513	-0.0276	-0.0721
C12	-0.1179	-0.0834	-0.1219	0.1633	0.3292
H13	0.1677	-0.0447	-0.0906	0.0416	0.0833
H14	0.1562	-0.0455	-0.0903	0.0461	0.0972
H15	0.1609	-0.0396	-0.0790	0.0330	0.0666
H16	0.2568	-0.0326	-0.0641	0.0262	0.0561
H17	0.2568	-0.0326	-0.0641	0.0262	0.0562
H18	0.1677	-0.0447	-0.0906	0.0416	0.0832
H19	0.1562	-0.0455	-0.0903	0.0461	0.0974
H20	0.1609	-0.0395	-0.0789	0.0330	0.0665

The second largest peak for the monomer represents a transition composed mainly by states H-3->L+1 and the third H->L+2 with the oscillator strength 1.0074 and 0.3475, respectively. For the dimer we have the second largest peak in an area of energy around 5.7 eV and oscillator strength of 1.2046, it

Figure 2. Neutral Absorption Spectra for PAzo. (1) monomer; (2) dimer and (3) trimer structures.



presents competition among the transitions H-4->L, H-6->L and H->L+4, and this last transition also appears among the more strong for the trimer, but with value of different energy, around 4.6 eV and with oscillator strength 0.6367. The transitions H->L+2 and H-2->L also appear with oscillator strength 0.188 and 0.1804 (3 and 4 peaks).

In the figure 3 we have the absorption spectrum of PAzo with charge +1 for the monomer, dimer and trimer and the strongest transitions continue being the transition composed mainly by H->L with oscillator strength 0.5379, 1.3885 and 1.1911. We have that the first optically activate transition between 1000 nm and 1800 nm, where we can see more clearly in the figure 4. In this figure we have the first optically activate transition in function of ring numbers present in the pyrrole molecule. Clearly we have the distinction among the two systems, neutral and under the effect of the polaron type defect. The neutral system show us a minimum energy gap of 2.5 eV. The other

Figure 3. Charge+1 Absorption Spectra for PAzo. (1) monomer; (2) dimer and (3) trimer structures.

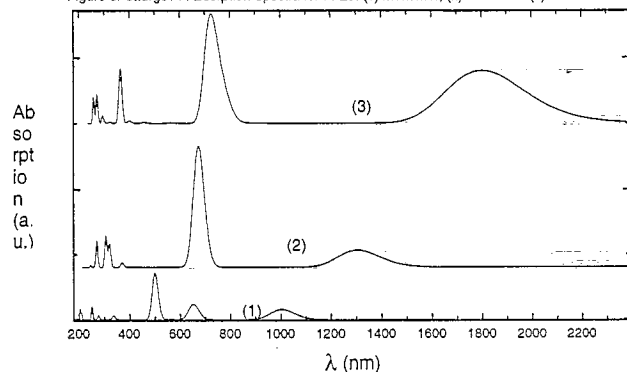
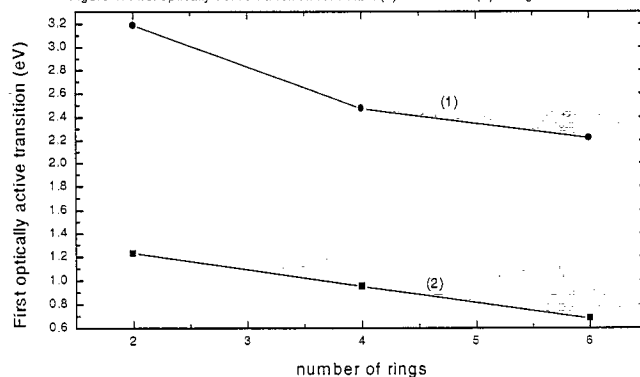


Figure 4. First optically active transition for PAzo. (1) neutral and (2) charge +1



curve show us that the polaron defect provokes a considerable red shift characterizing a narrow band gap materials.

3. Conclusion

1. The methodology utilized for the absorption spectrum simulation was shown in agreement when compared with the experimental results of the literature [1].
2. The comparative charge showed us that the polaron is defined in the area of the molecule.
3. The inclusion of the azo group in polypyrrole provoked significant decrease of the gap characterizing it as low band material gap.
4. The methodology was shown efficient for the design of new materials.

5. References

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