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Evolution of the Bipolaronic Structure in Going From One- to Two-Dimensional π Model Systems

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Long neutral and doubly charged oligodiacetylenes (with a maximum of 30 repeat units) as well as some of their aggregates have been studied in a semiempirical framework. By analyzing the plots of the one-electron ground-state density matrices, we have shown that the 12-units long oligomer is the borderline between two different behaviors of the electronic structure of the isolated charged systems. For oligomers shorter than this limit the bipolaronic structure is the dominant one, while for larger oligomers the polaron-pair structure is preferred. The major conclusion of this work concerns the effects of the interchain interactions in bipolaron systems, which are usually neglected in theoretical works. It is predicted that as a consequence of the latter in the bulk system a bipolaron generated on a single polymer chain will soon split into two polarons on adjacent chains.

1. Introduction

When compared to other organic compounds, conjugated molecules show unusual physical and chemical properties, such as relatively high charge mobility, fast nonlinear optical response, low optical absorption, high ease of oxidation and reduction, and others. The latter are correlated to the nature of their π-electron system, which consists of electrons of the sp^2-hybridized C atoms, described by the p$_z$ orbitals whose mutual overlap gives rise to a manifold of π molecular orbitals delocalized over the entire molecular backbone. In particular, the semiconducting properties of the conjugated polymers/oligomers, combined with their peculiar technological processability,[1] make them a new generation of materials suitable for a wide range of optoelectronic,[2] electronic,[3] and, more recently, biotechnological applications.[4] For these reasons, this class of materials is still now a testing bench for theoretical and experimental studies aimed to better understand, control, and design their physicochemical properties.

In this framework, a point that is still debated[5] is the formation of polaron and/or bipolaron species upon chemical doping, photo- or electro-chemical generation,[6] and in organic magnetoresistance effects.[7] Classically, the polaron (bipolaron) is described as the section of the backbone where the structural distortions, induced by the extraction or injection of one (two) electrons in the π-electron system, and the associated excess charge, are located.[8] The new features observed in the electronic spectra of the conjugated material after doping[8] are connected to the new electronic states originated by the generation of these species and their occupancy, and the intensity of the electron−phonon coupling determines their conduction and charge carrier mobility.[9] Knowledge of the relative stability of the polaron and bipolaron species is essential to predict the dominant structure in the charged system, and consequently to understand the properties of the modified material. As an example of a material on which a large body of such theoretical and experimental work has been performed, the polythiophene oligomers can be cited.[10] Nevertheless, few theoretical works have been devoted to study the effects, for example, of large substituents or of interchain interactions[11] in stabilizing or destabilizing the bipolaronic structure. In this work, we will address the importance of the second of the above factors in polydiacetylene oligomers. In fact, polydiacetylenes (PDAs) can be formed in single crystal, thin films, and solutions[12] by topochemical reactions mechanisms, and despite that PDA crystal cannot be easily doped,[13] a higher dopant concentration and efficient photo- or electro-chemical charge injections could be achieved in less crystalline systems, such as films,[14] which show interesting electronic and conductivity properties.[15] For these reasons, this class of conjugated oligomer/polymer can be of interest for their potential applications as optical materials.[16]

We chose unsubstituted oligodiacetylenes, *n*PDAs (where *n* is the number of repeat units in the oligomer), as models of one-dimensional conjugated π-systems, while the interchain interaction effects on the bipolaronic structure are studied on two different neutral or doubly charged clusters, named *a* and *b*, of three 15PDAs oligomers each, which can be seen as examples of two-dimensional π-systems. 15PDAs are chosen because they represent the shortest chain where the structural distortions induced by the charge injection begin to become stable in values and topology with respect to a further increase in the oligomer size. Because in technological applications conjugated systems are usually positively doped, and on the other hand we are constrained for the moment to consider only closed-shell singlet states (see below), here we will study positive bipolarons.

2. Computational Details

The geometries of the isolated, neutral, and doubly charged oligomers were obtained at the AM1 level using the MOPAC 6.0 software.[17] We outline that complete geometry optimization has been performed for all isolated neutral and doubly charged oligomers, without constraints or assumptions of any species.

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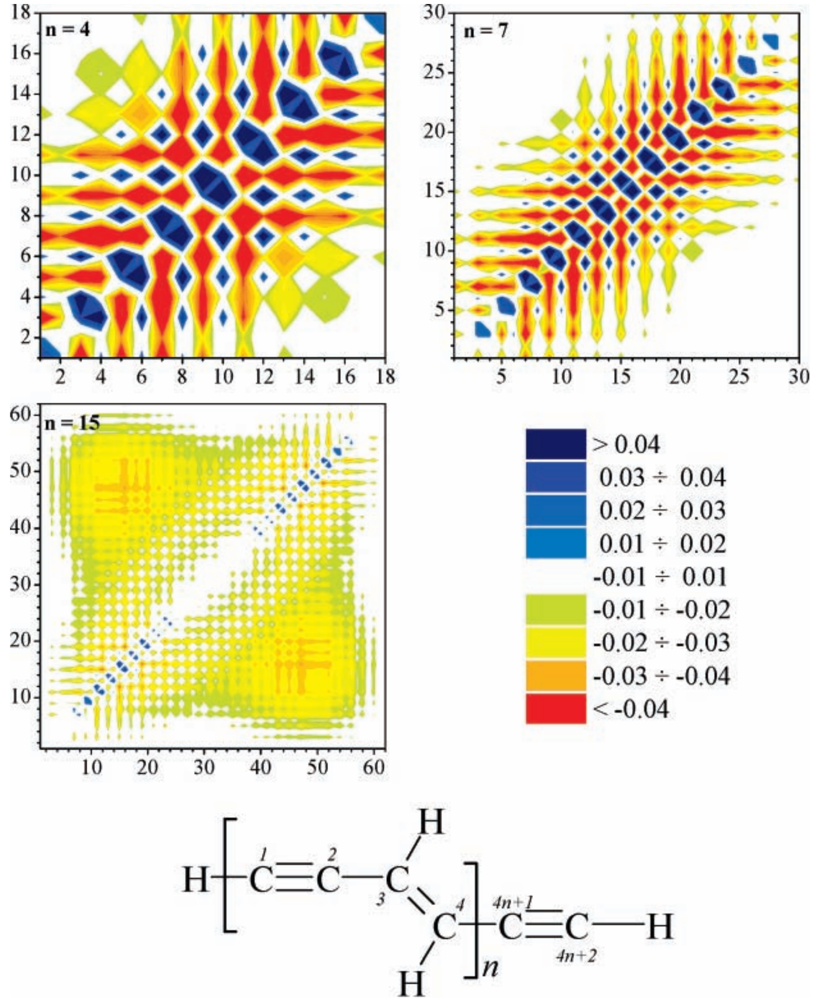

Figure 1. Contour plots of the difference between the one-electron ground-state density matrices of the neutral and the doubly charged *n*PDAs with $n = 4$, 7, and 15. Atom numbering is shown on the sketch at the bottom of the figure.

In the 15PDAs aggregates, each oligomer keeps its "isolated" neutral or doubly charged AM1 geometry, the neutral clusters including three "neutral" oligomers, and the doubly charged clusters including two "neutral" and one (the central one) "doubly charged" oligomer. Here, inverted commas refer only to the kind of AM1 geometry, the actual amount of charge on each oligomer being only determined by the global variational wavefunction. In cluster *a* (see below, Figure 2), the backbones lie on the same plane, while in cluster *b* they lie on three parallel planes in a cofacial arrangement, and the behavior of the electronic properties versus the interchain distance *R* is studied throughout. The choices of the cluster configurations and of the smallest interchain distances were made so as to model the properties of films (not of crystals, see ref 18).

The electronic properties are evaluated using the INDO/S Hamiltonian developed by Zerner and co-workers,[19] as implemented in the ZINDO package, to reduce as much as possible the computational resources required because of the large size of the aggregates. The nature of the electronic excitations of these systems (which are well known to be satisfactorily reproduced by the Zerner's parametrization) will be discussed in a forthcoming paper, where also energy effects referring to polaron/bipolaron equilibria will be thoroughly discussed. In the present work, we focus our attention on the one-electron ground-state density matrices (ρ_g) in the form of atomic and interatomic Mulliken populations. No guarantee exists that the AM1 method, while giving reliable theoretical geometries, is able to do the same with ground-state one-electron density matrices. On the contrary, the INDO/S method (as implemented for instance in the CEO approach,[20] being designed to give reliable transition density matrices as well as difference density matrices between them and the ground-state one) can be expected to behave well in this respect. We can give a graphical representation of ρ_g on a two-dimensional plot, where a suitably colored point represents the amount of the local population, and its x (y) coordinates the first (second) atom to which this population belongs. To be specific, the diagonal element ρ_{ii} of the plot is the net charge on the ith atom, while the off-diagonal element ρ_{ij}, as well as its symmetrical counterpart ρ_{ji}, is the fraction of the charge located between the ith and jth atom. The two-dimensional plot of the difference between the ground-state density matrices of a neutral molecular system and that of the same, but doubly charged, system shows how the excess charge is distributed all over the molecular system. This is strictly connected with the charge-induced geometrical distortion of the molecule, and the pictorial representation of this difference allows powerful correlations between bipolaronic structures in different oligomers or clusters.

3. Results and Discussion

The results obtained for a few one-dimensional π-conjugated model systems are shown in Figure 1, where the differences are plotted between the one-electron ground-state density matrices of the neutral and doubly positively charged *n*PDAs with $n = 4$, 7, and 15, respectively.

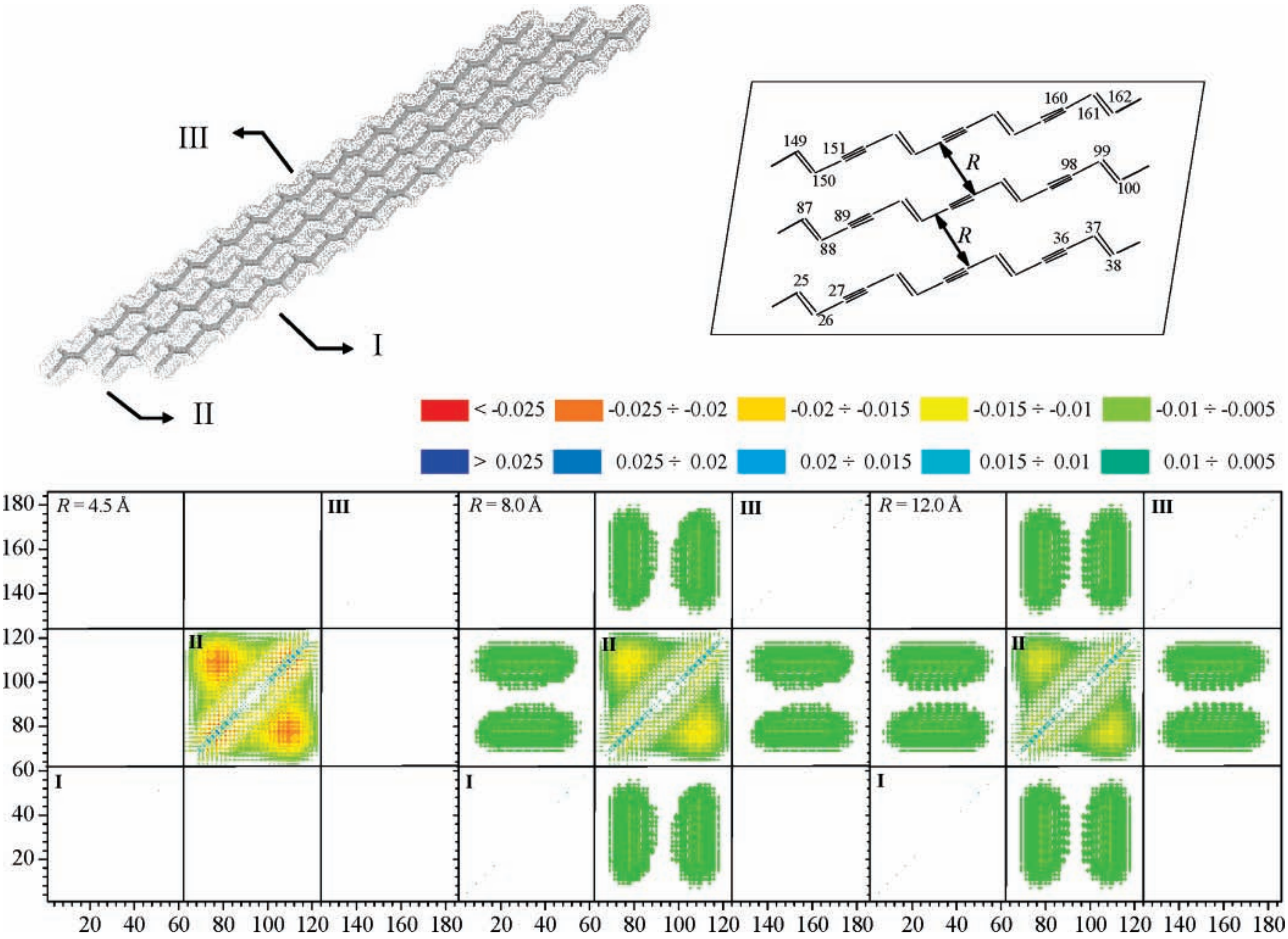

Figure 2. Contour plots of the difference between the one-electron ground-state density matrix of the neutral and that of the double charged cluster *a* at different interchain distances *R*. Atom numbering is depicted in the top left sketch.

The positive (negative) values in the figure indicate a partial decrease (increase) of the electron density in the charged oligomer with respect to the neutral one. For $n = 4$ and 7 (and for all $n < 13$), the excess charge is seen to be distributed over the whole backbone. The main contributions to the global charge (which we remind to be a doubly positive one) are due to the overlap electronic populations of atom pairs mainly involving central atoms, while the contributions decrease in moving toward the backbone ends. These pairs include C atoms belonging to double or triple bonds whose length variation (a lengthening due to the charge injection effects) can be nicely correlated with the corresponding (positive) variation in the electronic density. For the same reason, matrix elements referring to C atom pairs involved in single bonds (which shorten upon charge injection) can be seen to be negative. In other words, the $n = 4$ or 7 plots are in agreement with the "classical" picture of the bipolaron structure, in which the whole double charge is associated with the molecular moiety that undergoes the geometrical relaxation.

The plot of 15PDA exhibits a completely different behavior, showing along the diagonal two different and well-separated structures, which carry substantial variations in the density matrix elements. Each of the related moieties is centered in the middle of each half part of the molecule and corresponds to a backbone segment of about 14 C atoms, where the geometry change is located and to which about one positive charge is associated. It appears accordingly that in a sufficiently large oligomer two polarons (i.e., two molecular segments where the injection of a single charge induces geometry relaxation) are formed instead of a bipolaron. The two polarons are not isolated species, as clearly indicated by the presence of nonzero off-diagonal terms, which implies that an interaction between them occurs. The throughout negative sign of the latter density matrix elements means that there is an increase of the electronic density in the region between the polaron structures, that is, that a bonding condition between the two moieties takes place. By consequence, the plot in the panel $n = 15$ in Figure 1 is the picture of a spinless polaron pair,[8] due to the fact that in the present work we are considering only singlet states (see below). In the framework of the present description, the point where the transition between the above two different behaviors occurs can be seen to be $n = 12$ for unsubstituted oligodiacetylenes. For $n > 15$, no significant variations in the molecular geometry and in the electronic density are predicted (see Figure 1s of the Supporting Information). There is, however, some increase in the separation between the two moieties carrying the bond distortions, and up to 30PDA (the largest oligomer studied in this work) negative off-diagonal density matrix elements connecting in a bonding way the two polaron moieties are still present, although they decrease with increasing oligomer size. Similar results have been obtained in a recent work,[21] where a series of isolated unsubstituted oligothiophene dications (up to 50 repeat units) was studied at the DFT and ab initio CAS-SCF level. Note that in these systems the number of repeat units of the oligomer that lies at the borderline between the polaron and bipolaron domains results to be around 14, while in oligomers with $n \geq 30$ the two polarons are predicted to be independent species. Interestingly enough, the above authors, besides performing singlet closed-shell calculations just such as we did, also consider the singlet (and triplet) open-shell case, in which no electrons are constrained to be described by the same orbital, and two unpaired electrons in a dication can accordingly be believed to be even more free to separate. Their results show that the (RB3LYP-UB3LYP) energy difference amounts at most to some 0.2 eV, while the forms of the charge distribution and of the geometry distortions are very similar to ours, with only a very small increase of the effects in the open-shell case.

The above results refer to isolated oligomer chains, as is often done in theoretical work. In the following, we shall overcome this limitation, and we will study how the one-electron density matrix of a charged oligomer is affected by interchain interactions. The latter are modeled by adding two neutral neighbor chains so as to build the two different kinds of clusters described in section 2. The difference between the ground-state one-electron density matrix of the neutral cluster and that of the charged one is depicted in Figures 2 and 2s (given in the Supporting Information) for clusters *a* and *b*, respectively.

In the top of Figure 2, the cluster *a* morphology (left) and the atom numbering (right) are depicted, and the subsequent plots show the topologies of the density matrix variation for three different values of the interchain separation (R). For $R =$ 4.5 Å (the interchain distance corresponding to the contact between the oligomers van der Waals surfaces), almost all of the excess charge is seen to be confined on unit II (the central one), and its distribution is close to that of the isolated chain. This is because the potential well created by the relaxed geometry of unit II (which is the geometry of the isolated doubly charged chain) is effective in this case in constraining the polaron-pair on the central unit, because the cluster arrangement does not allow substantial interactions between the p_z orbitals belonging to different neighbor chains and perpendicular to their molecular planes. The effect of the chain orientation is apparent by looking to the corresponding case of cluster *b* (panel $R =$ 3.0 Å of Figure 2s) where the bond order of the polaron pair is destroyed, and strong interactions involving all of the p_z orbitals of the cluster units arise. As a consequence, the potential well created by the relaxed geometry of the central unit gets reduced, and a sensible fraction of the excess charge (about 19%) can be spread out over the two external units. What is somewhat unexpected is that the increase of the interchain distance causes the interaction between units II and I(III) to increase, as shown in panels $R =$ 8.0 and 12.0 Å of Figure 2 (similar is the picture in Figure 2s) by the significant contributions to the electron density given by the off-diagonal blocks. We remind in this respect that the diagonal blocks depict how the one-electron density is located on the molecular units of the cluster, while the off-diagonal ones are related to the interactions between the units. To this increase of the off-diagonal matrix elements corresponds a decrease of the bonding order of the polaron pair in the central unit, and on the whole a decrease of the fraction of the excess charge, which is confined on the central unit itself. After passing through a minimum, the latter becomes again 100% for $R >$ 36 Å, and the corresponding plots of the one-electron ground-state density matrix are essentially equal to that in the panel $R =$ 4.5 Å of Figure 2. We have checked this trend against DFT calculations at the B3LYP/6-31G level, whose results are compared to the AM1 ones in Table 1.

The transfer of the excess charge from the central to the neighbor chains predicted by the semiempirical calculations is not only nicely confirmed but results to be further increased. Also the trend of the excess charge with increasing R is confirmed and even magnified for cluster *b*, while for cluster *a* the DFT charge on every unit is nearly constant (except for very large R). These findings (as well as those in ref 21) support the idea that neither the zero differential overlap approximation nor the neglect of electron correlation effects affects in an important way our AM1 and INDO/S ground-state results.

TABLE 1: Distribution of the Excess Charge[a] on the Molecular Units of Clusters *a* and *b*, Computed at the Semiempirical (AM1) and DFT (B3LYP/6-31G) Levels for Different Interchain Distances (*R*)

Cluster *a*

	AM1		B3LYP/6-31G	
R (Å)	I (III)	II	I (III)	II
4.50	0.02	1.95	0.70	0.60
8.00	0.45	1.10	0.66	0.68
12.00	0.47	1.06	0.66	0.68
36.00	0.00	2.00	0.00	2.00

Cluster *b*

	AM1		B3LYP/6-31G	
R (Å)	I (III)	II	I (III)	II
3.00	0.51	0.98	0.55	0.90
5.00	0.06	1.88	0.59	0.82
8.00	0.36	1.27	0.64	0.72
12.00	0.50	1.00	0.65	0.70
36.00	0.00	2.00	0.00	2.00

[a] Evaluated as Mulliken charge.

In conclusion, the above results clearly indicate that the intermolecular interactions act so as to screen the (intramolecular) interaction between the two polaron moieties on the central unit. Keeping in mind that in our clusters the geometry of the central and of the neighbor units are constrained to be those of the doubly charged and of the neutral isolated oligomers, respectively, it is clear that the situation predicted here can be considered as the initial trend of a process that will cause the splitting of the polaron pair, generated on a single chain, into two polarons on two different oligomers.

4. Conclusion

Our study of the nature of the dication species on long oligodiacetylenes, based on the analysis of the one-electron ground-state density matrix of neutral and double charged systems, shows that for short isolated oligomers (less than 12 repeat units) the electronic structure of the positively doubly charged oligodiacetylene is the bipolaronic one, while for larger isolated oligomers (more than 12 repeat units) it admits the presence of a polaron pair in which the two polaron species are connected by a ligand bond order, which is still present up to oligomers with 30 repeat units.

When interchain effects are included, our results predict an unexpected trend in the electronic structure of the charged species, which can be of importance in determining the properties of an oligodiacetylene bulk. In particular, the presence of neighbor chains within a distance R of about 30−36 Å acts so as to dissociate the polaron pair into two polarons lying on two different oligomer chains, while for higher R values the polaron pair remains confined on the molecular unit where it has been generated. This implies a variable behavior of the charged species generated on the polymer bulk (and consequently of the charge carrier and of their mobility) as a function of the backbone separation, which can widely vary especially when the oligomers are substituted with large alkyl groups, as is often done to improve solubility.

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Supporting Information Available: Figure 1s: Contour plot of the difference between the one-electron ground-state density matrix for the neutral and double charged 30PDAs. Figure 2s: Charged cluster *b* at different interchain distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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