A new class of push–pull molecules for molecular electronics

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Abstract

In this work, we have found that large conjugated pyridinium betaines, molecules composed by a donor (D) and acceptor (A) pair connected through a long conjugated chain, exhibit an inversion in the expected direction of the electron transfer resulting from photo-excitation. Once the connecting bridge is increased beyond a given size, the electron transfer is predicted to occur in a reversed manner, i.e. from the acceptor to the donor side of the molecule. This effect seems to be associated to an inversion of the spatial localization of the frontier molecular orbitals. We present results for the spatial localization of the frontier molecular orbitals and the theoretical absorption spectra of members of increasing size of a specific family of pyridinium betaines.
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1. Introduction

By betaine, one designates not only the $[(CH_3)_3 N^+ CH_2 COO^-]$ molecule (a naturally occurring zwitterion), but also several quaternary ammonium salts analogous in structure. Pyridinium betaines are good candidates for the design of photoactive molecular assemblies and the preparation of LB films with intense NLO response.

As we known, biological activity is directly correlate to molecular shapes [1,2], such as size and electronic transitions. Also, it is well-known [3] that the correlation of biological molecules can be strongly dependent on the electrostatic fields generated in the process of charge transfer. Those fields are determined by structural molecular factors [4]. Since measurements of conformation data are not yet available for this molecule, we will have to rely on simulation information gathered from electronic structure calculations.

Small pyridinium betaines have large molecular hyperpolarizabilities relative to their molecular sizes [5]. We have examined the electronic and nonlinear optical properties of several families of betaine compounds [6].

In this communication, we report the most important results found for one of these families (Fig. 1), where a given pair of D and A groups is connected through conjugated bridges of increasing sizes.

2. Methodology

Since experimental data are not available for the geometries of the molecules investigated (Fig. 1), systematic geometry optimizations were required. Sophisticated semiempirical methods such as AM1 (Austin method 1), and PM3 (parametric method 3) provide a good balance between quality and computational effort to treat organic compounds.

While geometric and basic electronic features, such as bond lengths, bond and dihedrals angles, heats of formation, dipole moment values, etc., are well described at AM1 and PM3 levels, excitation electronic energies are usually overestimated, as expected from zero differential overlap (ZDO) methods that do not include configuration interaction (CI) corrections.

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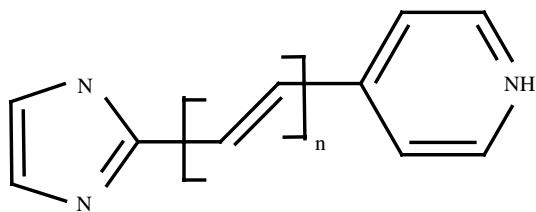 *E-mail address:* jordan@ufpa.br (J.D. Nero).

Fig. 1. Members of the family of pyridinium betaines investigated had an increasing number n of double bonds in the connecting conjugated bridge.

After the determination of optimized geometry, the absorption spectrum of each molecule was simulated by the INDO/S-CI (intermediate neglect of differential overlap/spectroscopic-configuration interaction) [7–10], with parameters chosen to give the best description of the UV-NIS-Visible optical transitions [11–14] and 121 configurations were investigated for each molecule, including singlet states. We have taken account from the first 10-UMOs (unoccupied molecular orbitals) to the last 10-OMOs (occupied molecular orbitals) and adopted the Mattaga–Nishimoto γ's.
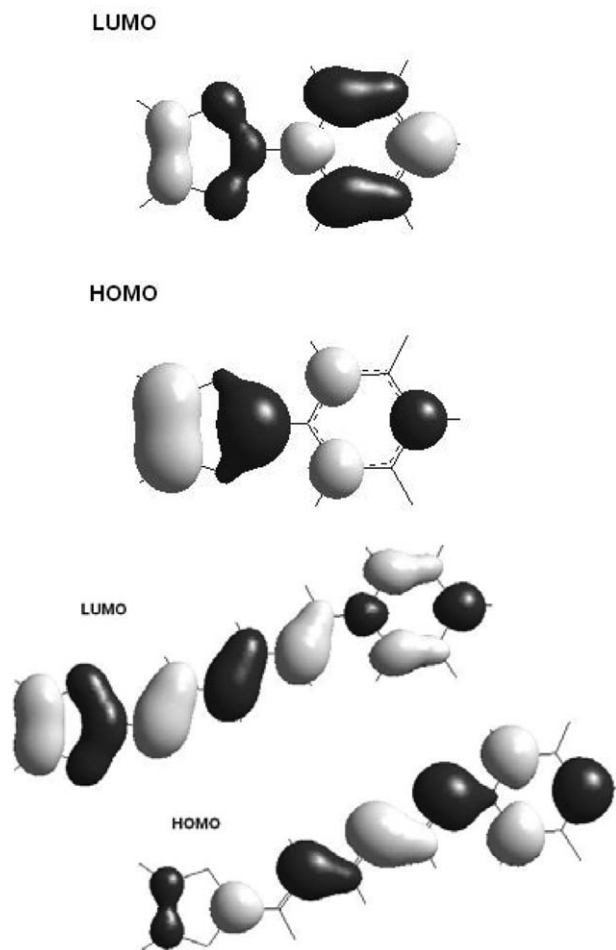

Fig. 2. Schematic representation of the calculated HOMO and LUMO for the $n = 0, 1, 2, 3, 4$ and 5 members of the betaine family considered.
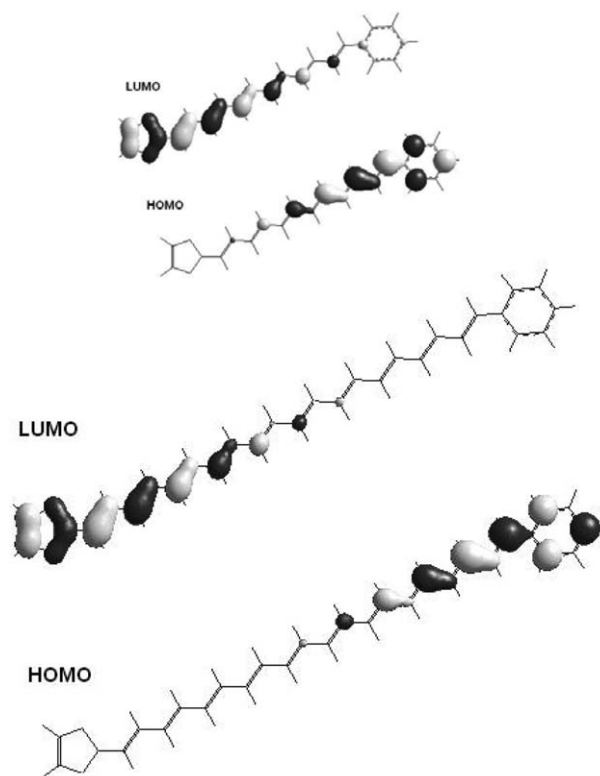

Fig. 3. Schematic representation of the calculated HOMO and LUMO for the $n = 6, 7, 8, 9$ and 10 members of the betaine family considered.

Also, we adopted well-known methodology for the prediction of the nonlinear polarizabilities (hyperpolarizability) presented elsewhere [15,16].

3. Results and discussion

Preliminary results in the investigation of the electronic structure of several pyridinium betaines [2] using semiempirical quantum chemical methods has revealed a very peculiar reversal of the charge transfer for the large molecules of each family. In this communication, we will show that this unusual behavior seems to be associated to a progressive change in the spatial localization of the frontier molecular orbitals (FMO) of the molecules that follows the increase in the size of the conjugated bridge connecting the D and A groups. For the smaller molecules of each family, the HOMO [LUMO] is more localized in the extremity of the molecule containing the D [A] group. In Fig. 2 we show the HOMO and LUMO representations for the smallest member (i.e. when the D and A groups are directly attached) and for $n = 2$ of the family represented in Fig. 1.

As it is shown in Fig. 3 for the $n = 6$ and $n = 10$ molecules, a definite inversion of the spatial localization of the HOMO and LUMO takes place beyond a certain length of the conjugated bridge (It is possible to see the inversion process on the reference.[1] As a consequence, one can expect

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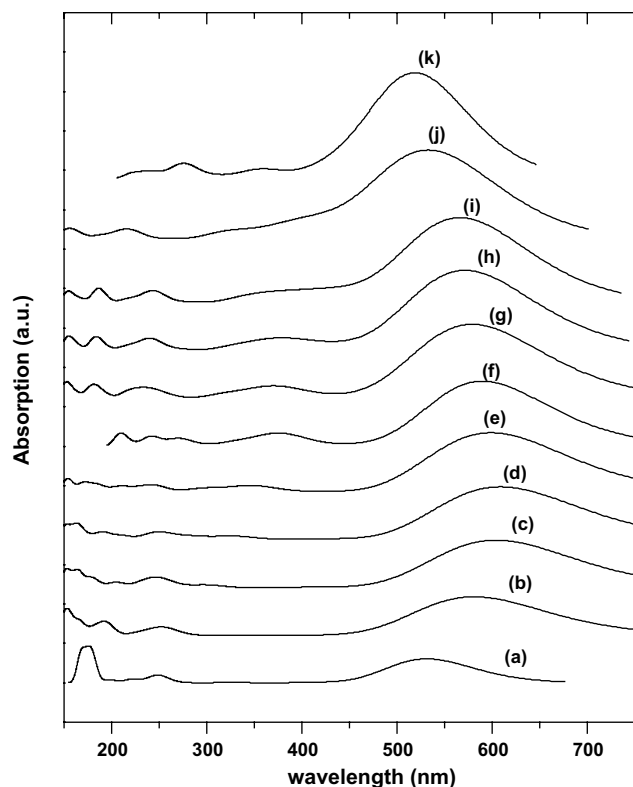[1] The supplementary file has more FMO's.

Fig. 4. Full INDO/S-CI theoretical absorption spectra of the $n = 0$ (a), $n = 1$ (b), $n = 2$ (c), $n = 3$ (d), $n = 4$ (e), $n = 5$ (f), $n = 6$ (g), $n = 7$ (h), $n = 8$ (i), $n = 9$ (j) and $n = 10$ (k), members of the betaine family considered calculated for the optimized geometries.

94 several unusual properties to be associated to these mole-
95 cules, such as, for instance, a reversed photoinduced elec-
96 tron transfer, i.e. following light excitation, charge will be
97 transferred from the acceptor to the donor group.
98 In Fig. 4 we plot the INDO/S-CI theoretical (gas phase)
99 absorption spectra of some members of the family of
100 betaines investigated. For the smallest molecule ($n = 0$)

(Fig. 4a), we predict the existence of three main bands cen- 101
tered at ≈ 530 nm, 250 nm and 175 nm. For the member 102
with $n = 5$ (Fig. 4f), we estimate that there will occur an 103
increase in the intensity of the first band, while the second 104
one is split in two. Finally, for $n = 10$, i.e. after the inver- 105
sion of the FMO has completely taken place, a blue shift 106
of the main band is found (Fig. 4k). Details of the main 107
predicted transitions are shown in Table 1. 108
In Table 1 we have the main transition for all molecules. 109
It is possible to see the inclusion of HOMO to LUMO + 1 110
for $n = 6$ to $n = 9$. It gives *two very important pattern*: (i) 111
Red shift on absorption spectra from $n = 0$ to $n = 5$ (from 112
Fig. 4a–f) and main transition is HOMO to LUMO; (ii) 113

Table 1
Principal electronic UV-NIS-Vis absorption transitions as determined from INDO/S-CI calculations based on the optimized ground-state geometry from $n = 0$ to $n = 10$ members of the betaine family considered

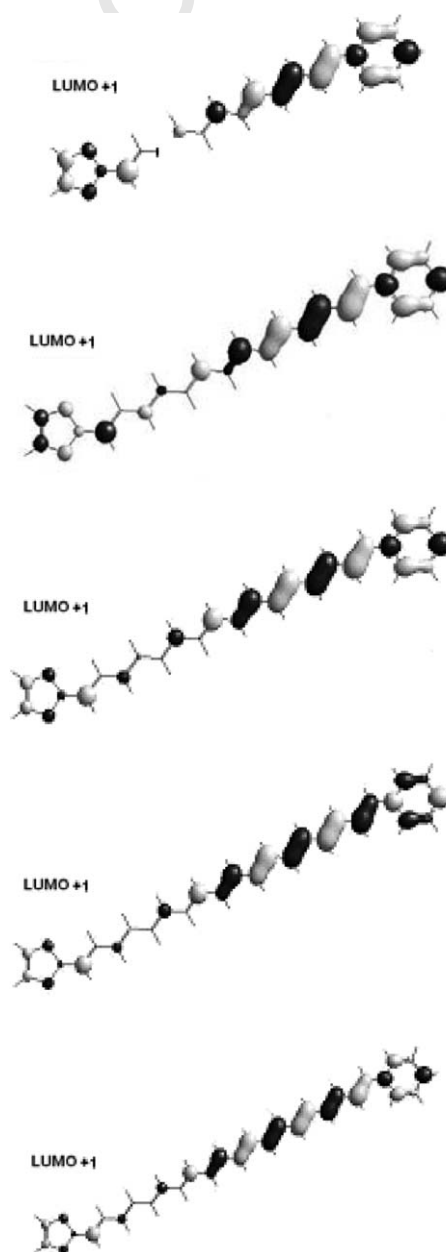| # //	o.s. (a.u.)	Absorption transitions
0	0.76	$0.99 \ |H \rightarrow L\rangle$
1	3.94	$0.69 \ |H \rightarrow L\rangle$
2	1.90	$0.68 \ |H \rightarrow L\rangle$
3	2.14	$-0.68 \ |H \rightarrow L\rangle$
4	2.41	$0.67 \ |H \rightarrow L\rangle$
5	2.69	$0.63 \ |H \rightarrow L\rangle$
6	2.96	$-0.56 \ |H \rightarrow L\rangle$
		$0.34 \ |H \rightarrow L + 1\rangle$
7	3.22	$0.48 \ |H \rightarrow L\rangle$
		$0.44 \ |H \rightarrow L + 1\rangle$
8	3.42	$0.40 \ |H \rightarrow L\rangle$
		$0.52 \ |H \rightarrow L + 1\rangle$
9	3.58	$-0.32 \ |H \rightarrow L\rangle$
		$-0.57 \ |H \rightarrow L + 1\rangle$
10	3.71	$-0.60 \ |H \rightarrow L + 1\rangle$

Fig. 5. Schematic representation of the calculated LUMO + 1 for the $n = 6, 7, 8, 9$ and 10 members of the betaine family considered.
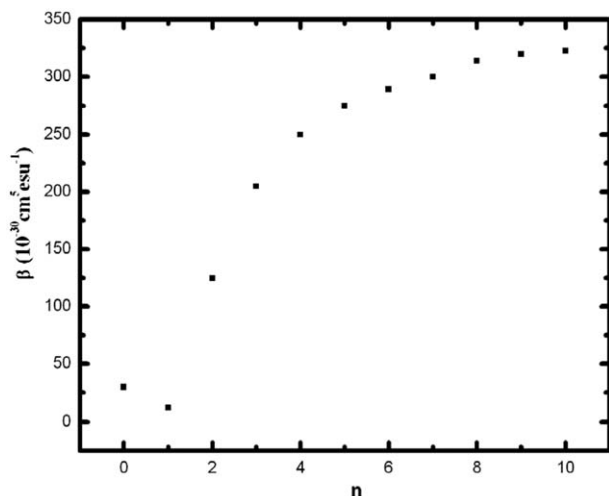
Fig. 6. Hyperpolarizability of betaine family considered.

114 Blue shift on absorption spectra from $n = 6$ to $n = 9$ (from
115 Fig. 4g–j) and main transition is composed by two species
116 (HOMO to LUMO and HOMO to LUMO + 1). Finally
117 only HOMO to LUMO + 1 for $n = 10$.
118   To clarify above results, in Fig. 5 it is possible to see
119 LUMO + 1 for $n = 6, 7, 8, 9, 10$. These results have similar
120 behavior with LUMO ($1 < n < 6$).
121   It could be expected a change of behavior on hyperpo-
122 larizability but in Fig. 6 it is presented and a canonical pat-
123 tern were founded.
124   To exclude the possibility of contamination of the
125 results as an artifact of the quantum chemical method used,
126 we have repeated these calculations using different method-
127 ologies. The existence of the predicted reversal in the spa-
128 tial localization of these FMO was confirmed in all cases.

129 **4. Conclusions**

130   As an example of a new effect predicted to occur in large
131 pyridinium betaines we present results for a specific family
132 of these compounds. For the largest molecules we have
133 found that there is in fact an inversion of the spatial local-

ization of the FMO. This is expected to have important 134
consequences not only on the optical, but also on several 135
other electronic properties of these betaines, which consti- 136
tute a new class of push–pull systems. This work is part of a 137
more complete investigation of the ground and excited 138
states of betaines to be reported elsewhere and at the 139
moment we are doing simulations applying external electric 140
field. 141

Appendix A. Supplementary data 146

Supplementary data associated with this article can be 147
found, in the online version, at doi:10.1016/j.optmat. 148
2006.03.035. 149

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