

Comment on ‘Polaron formation and symmetry breaking’ by L. Zuppiroli et al. [Chem. Phys. Lett. 374 (2003) 7]

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Abstract

L. Zuppiroli et al. [Chem. Phys. Lett. 374 (2003) 7] have theoretically studied polaron formation in oligo(phenylene vinylene) radical ions. In particular, they obtained with the AM1/UHF method a stepwise increase of the relaxation energy with increasing chain length. In this Comment, we suggest that this result is likely to be an artifact. We argue that UHF is particularly inappropriate for studying energies of open-shell pi-conjugated systems because of inherent spin contamination leading to wrong molecular structures. We show that, within the AM1 methodology, relaxation energies are rather insensitive to chain length and discuss the origin of this behavior.

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It is generally expected that the injection of one charge (electron or hole) into conjugated oligomers and polymers induces significant local geometric changes as a result of their strong electron-vibrations coupling [1,2]. This self-trapping of charge and spin leads to the formation of a so-called polaron in condensed-matter physics terminology. The polaron relaxation (binding) energy, defined as the difference between the total energy of the radical-cation in the neutral geometry and that in its fully relaxed geometry, is an important parameter governing charge transport processes in conjugated materials [3–5].

In a recent Letter [6], Zuppiroli et al. have theoretically studied the energetics of polaron formation in oligo(phenylenevinylene)s (OPVs) at the Density Functional Theory (DFT) and semi-empirical Austin Model

1 (AM1) levels. Their DFT results confirm the absence of self-localization of the charged species at this level of theory, as previously suggested by other theoretical studies [7,8], and provide increasingly small relaxation energies (from ~0.15 to 0.05 eV in going from oligomers with two to eight rings). In contrast, their AM1 calculations yield relaxation energies that are small (less than 0.1 eV) up to six [five] rings for cations [anions] and suddenly increase in a step-like fashion up to 0.3 eV in longer chains.

The AM1 results of Zuppiroli et al. contradict our own findings obtained with the same approach on OPV radical-cations both in terms of absolute relaxation energy values and chain-length evolution. It is the goal of this Comment to illustrate and discuss the major differences present between the two sets of data. We stress that this Comment is not intended to address the extent to which the AM1 Hamiltonian is applicable to the description of polaron formation in conjugated chains; our aim is to establish internal consistency among results published within the same methodology,

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as far as geometries and relaxation energies are concerned.

We have carried out AM1 calculations with the AMPAC 6.55 package [9]. We checked the impact on the optimised geometry of coupling the AM1 method to a full configuration interaction scheme within a complete active space (CAS) of variable size. We found this impact to be very weak for both neutral and singly charged molecules, as their wavefunctions are systematically dominated by the ground-state determinant. While Zuppiroli et al. used exclusively the AM1/UHF (Unrestricted Hartree–Fock) formalism to describe the radical-cations [10], we have calculated the energies of the unrelaxed and fully equilibrated radical-cations with AM1 at the UHF, ROHF (Restricted Open-shell Hartree Fock), and ROHF/CAS4 (where the highest two occupied and lowest two unoccupied molecular orbitals are included in the active space) levels. In order to address the role of torsions along the backbone, we have performed both full geometry optimizations (starting from non-planar structures) and optimizations where complete planarity of the molecules is imposed.

Fig. 1 displays the chain-length evolution of the relaxation energies obtained with the various approaches. Fig. 2 describes the AM1/ROHF radical-cation geometric structures using as a relevant descriptor the length of the double bonds in the vinylenic linkages. At the AM1/ROHF level, the C–C bond lengths in the chain segment where the charge resides change by up to 0.02–0.03 Å in the phenylene rings (that acquire a quinoid character) and by up to 0.04–0.05 Å in the vinylenic units (thereby strongly decreasing the degree of C–C bond-length alternation). The ROHF and ROHF/CAS4 relaxation energies are very similar (which is as expected since their wavefunctions practically coin-

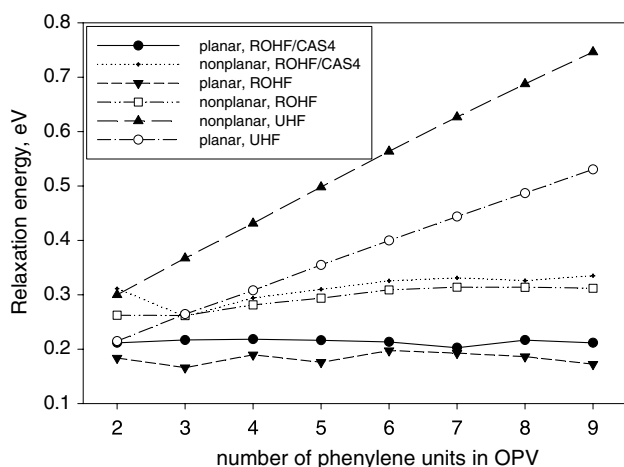


Fig. 1. AM1 (AMPAC) relaxation energy in OPV radical cations constrained planar and unconstrained (nonplanar when neutral) as a function of chain length ($n = 2$ corresponds to stilbene) as obtained within different ansatz schemes (ROHF, ROHF/CAS4, UHF).

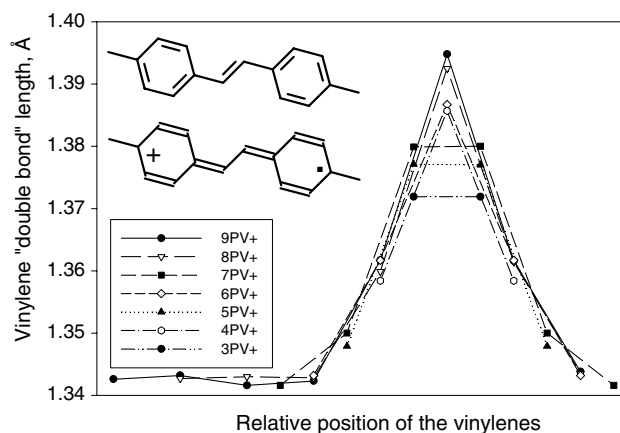


Fig. 2. Polaronic distortion in AM1/CAS4 geometry of planar OPV radical cations as represented by vinylenic bond lengths along the chain, the shortest in the middle of the polaron.

cide) and are little affected by chain length. The AM1 calculations yield torsion angles between the planes of the phenylene and vinylenic units of some 20° for neutral OPVs; this is consistent with previous *ab initio* Hartree–Fock calculations [11–13]. We note that in all these calculations the torsional potential energy curve is very flat around the planar conformation and that very recent post-HF calculations provide a planar conformation for trans-stilbene [14], in agreement with experimental data from fluorescence spectra in ultra-cold collision-free molecular beam [15,16]. In the radical-cations, the chain becomes fully planar around the polaronic defect; this rationalizes the increase in relaxation energy when going as a starting point from constrained (planar) to fully relaxed (twisted) chains. It is possible to deduce the length of the geometric distortion associated to a polaron from the width of the planarized segment of the chain. The calculations indicate that width to be about 4 phenylene rings. This is consistent with the width of the spin distribution deduced from ENDOR experiments on PPV chains supporting polarons [17].

The relaxation energy is estimated to be on the order of 0.2 eV for molecules restricted to planarity and around 0.3 eV when fully optimized at the AM1 level. Thus, the very small relaxation energies reported by Zuppiroli et al. for the shortest chains are not reproduced. It is clear from Fig. 2 that the geometry relaxation is very pronounced in the shortest chains for which the polaron extension is not complete. We observe that the amplitude of the local geometric distortions increases gradually with chain length until polaron formation is complete; large relaxation energies saturating rapidly with chain size thus reflect the geometric evolution characteristic of spin-restricted calculations (that appear to lead to somewhat underestimated polaron extensions [18]). We note that the value of about 0.2 eV obtained for polarons in planar chains has the same order of magnitude as the singlet exciton

relaxation energy calculated in a planar conformation at the AM1/CI level [19]; this feature is rationalized by the fact that the two relaxed species display very similar geometry deformations. Theoretical fits of the vibronic structure observed in the absorption and emission spectra of conjugated compounds can also be achieved to extract Huang–Rhys factors and estimate exciton relaxation energies. Such an analysis has been performed for the emission spectra of OPVs containing from 3 to 5 rings [20]; this yields a small evolution with chain size (0.21, 0.19, 0.17 eV for the 3-, 4-, and 5-OPVs, respectively, which is in good agreement with the present results).

AM1 geometry optimizations performed without symmetry constraints yield symmetric structures for short chains, with a truncated polaron centered in the middle of the chain alternatively on a vinylene or a phenylene unit according to chain size. In longer chains (beyond 7 rings), the polaron systematically centers on a vinylene linkage, in agreement with the interpretation of the ENDOR spectra of photoinduced polarons in PPV [17], and localizes near one chain end (see Fig. 2a); the energy required to translate the polaron along the backbone is, however, very small. When this stage is reached, the geometry of the chain segment supporting the polaron no longer evolves when the oligomer gets longer; increasing the chain length only adds more segments that do not participate in the relaxation process and thus remain in the neutral geometry. We emphasize that the polaron localization (and corresponding rupture of symmetry) is not associated with any sharp change in the local geometry of the defect and hence in the relaxation energy compared to shorter radical-cations.

An important aspect is that the chain-length evolution of the relaxation energy obtained at the AM1/UHF level is completely different when compared to that provided by spin-restricted methods. While the value estimated for stilbene is similar for AM1/UHF and AM1/ROHF calculations, the relaxation energy at the UHF level keeps increasing linearly with increasing chain length. We stress that the UHF results obtained here are different from those of Zuppiroli et al. [6]. We suggest that this discrepancy is to be attributed to the fact that the latter values have been obtained with the AM1 Hamiltonian using the MOPAC93 package [10]. We found that MOPAC93 turns out to provide total energies higher than those of AMPAC 6.55 for non-relaxed radical-cation structures only at those chain lengths for which decreased relaxation energies were consequently obtained in [6].

This non-systematic upward energy shift might reflect MOPAC93 convergence problems for these molecules.

The main advantage of spin-unrestricted methods for the description of radicals is their ability to yield the distribution of both α and β spin components. Further-

more, an UHF wavefunction can present a lower symmetry than the molecular point group, this electronic symmetry breaking being often a precursor to spatial symmetry breaking [21]. This is for instance illustrated by the fact that a positive charge injected in an unrelaxed five-ring OPV (i.e., displaying the geometry of the neutral molecule) centers on a vinylene unit although a phenylene ring lies in the middle of the molecule; this confirms the tendency for polarons to localize over a vinylene linkage in long chains. However, it is also well established that UHF provides incorrect trends in long conjugated molecules; this is illustrated for instance by the fact that in polyene chains, UHF tends to equalize single and double bonds, thus unpairing the π -electrons, and completely delocalizes neutral radicals [18,22]. A pronounced charge localization is observed in OPV radical-cations at the AM1/UHF level; however, the geometry of the segments surrounding the defect never reaches the structure characteristic of the neutral state. In connection to this observation, the spin contamination increases linearly with chain length, which reflects the increasing number of bonds that are described incorrectly. Thus, the UHF relaxation energies appear to be directly correlated with spin contamination, as shown in Fig. 3; which strongly suggests that there exists a close relationship between these two parameters. Note that the correct value of $\langle S^2 \rangle$ for the doublet ($S = 1/2$) is $S(S + 1) = 3/4$ independent of the chain length.

In conclusion, we have carried out a thorough analysis of the AM1 relaxation energies in oligo(phenyl-enevinylene) radical-cations. We have reinvestigated the results obtained at the UHF level by Zuppiroli et al. [6] and compared them with those obtained at the ROHF and ROHF-CAS4 levels. Our work (i) reveals package-dependent discrepancies in the UHF results and (ii) shows that the UHF relaxation energies obtained for radical-cations are not reliable due to the erroneous

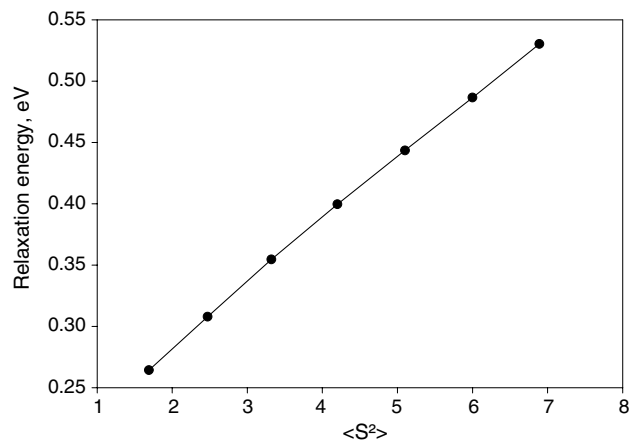


Fig. 3. AM1/UHF relaxation energy in planar OPV radical cations plotted vs. $\langle S^2 \rangle$: linear correlation with spin contamination.

(spin-contaminated) description of the chain segments outside the polaron defect that remain in the neutral geometry.

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