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Adiabatic One- and Two-Photon Excited States in Phenylene-Based Conjugated Oligomers: A Quantum-Chemical Study

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Four series of conjugated oligomers are studied by AM1-CAS-CI method with the purpose to describe the adiabatic lowest one- and two-photon excited states. Polyenes where the lowest singlet is of even parity ($S_1 = 2A_g$) serve as test for the accuracy of the approach. Oligomers of *p*-phenylenevinylene (PV_n), *p*-phenylene (PP_n) and *p*-phenyleneethynylene (PE_n) with up to $n = 6$ aromatic rings are taken as prototypes of luminescent conjugated systems where S_1 is dipole-allowed. One-photon excitation energies (E) are found to follow closely the linear E vs $1/n$ rule, unlike polyenes where the slope is steeper. The lowest two-photon excited state in PV_6, PP_6 and PE_6 is by at least 0.5 eV higher in energy than the dipole-allowed one. The former bears relation to $2A_g$ in polyenes, except for PE where a dipole-forbidden singly excited state approaches $1B_u$ faster. Relaxation energies are typically smaller than those in polyenes, and decrease with n. For the one-photon exciton they increase from PE to PV to PP, but fall too short to explain the Stokes' shift in the latter.

1. Introduction

The quasi-one-dimensional nature renders the excited states in conjugated polymers localized and profoundly different from those in solid-state semiconductors.[1] A pivotal role is played by *trans*-polyacetylene (PA) where strong electron−lattice ($\pi-\sigma$) coupling alone produces an electronic gap. The resulting degenerate ground state supports solitons as elementary excitations, and no difference is made between neutral and charged ones as long as $\pi-\pi$ interactions are neglected. Thus, the noninteracting model of Su, Schrieffer and Heeger (SSH)[2] explains most features of PA,[3] except the presence of an even-parity excited singlet $S_1 = 2A_g$[4] beneath the one-photon threshold: a phenomenon associated with electron correlation.

The incorporation of aromatic rings in the conjugated chain like in poly(*p*-phenylene) (PPP), poly(*p*-phenylenevinylene) (PPV), and poly(*p*-phenyleneethynylene) (PPE), lifts the ground-state degeneracy and decreases the effective electron−phonon coupling.[5] Nevertheless, excited states are still outlined as exciton−polarons[6] to stress that structural relaxations are no less essential than Coulomb interactions. The juxtaposition of PA and nondegenerate conjugated polymers goes further by noticing that the latter are typically luminescent. Therein, S_1 is strongly one-photon allowed while the two-photon excited states of ground-state symmetry remain above it. The different ordering of the lowest excited states in PA and phenylene-based polymers is rationalized[7] in terms of the π-correlated Peierls−Hubbard model by invoking the concept of strong virtual bond alternation[8] introduced by aromatic rings. A more comprehensive treatment of π-correlations[9] is limited to numerical results for finite systems. The necessity to consider $\pi-\sigma$ coupling explicitly typically limits configuration interaction to single excitations (CI-singles) allowing the description of odd-parity exciton−polarons in a nanoscopic scale.[10] When CI-doubles have to be included to describe two-photon excited states (even-parity excitons), the size of the systems feasible is reduced again.[11]

Nowadays, it is generally recognized that both electron−lattice coupling and electron correlation play an important role in conjugated polymers. However, practicable models (e.g., SSH, Hubbard) summon explicitly either the first or the second ingredient only, and therefore concentrate on explaining different types of phenomena. A more adequate treatment, namely, the description of adiabatic excited states with electron correlation accounted for, is only accessible for finite-sized systems. Therefore, the molecular approach focusing on conjugated oligomers of increasing length has gained credit not only experimentally,[12] but as a theoretical tool,[13] as well. The main practical advantage from the latter perspective is the use of less approximate methods with good record for molecules. This is particularly important for polymers with local ring-torsional degrees of freedom like PPP and PPV. Ring torsions couple with π-conjugation and take part in the structural relaxations of the excited states, but remain beyond the scope of simple electron−phonon coupling schemes, or require case-specific treatment.[14] Hence, all-valence-electron semiempirical molecular models have been widely used in the interpretation of the photophysics of oligomers of PPV, PPP and other conjugated polymers. Brédas and co-workers have performed a series of detailed quantum-chemical studies on the excitations in oligo(*p*-phenylenevinylenes),[15] including consideration of substitution and aggregation effects.[16] The binding energy of the odd-parity excitons in PPV has been extensively debated both from the experimental[17] and theoretical[18] perspective. Oligo(*p*-phenylenes) have also been considered[9,19,20] theoretically at different levels of sophistication. These numerous studies focus predominantly on the dipole-allowed excited states that are responsible for photo- and electroluminescence in nondegenerate polymers. Two-photon excited states are essential for nonlinear optical response, but they have been typically described[9,19,21] in vertical approximation, neglecting structural relaxations. Indeed, electron

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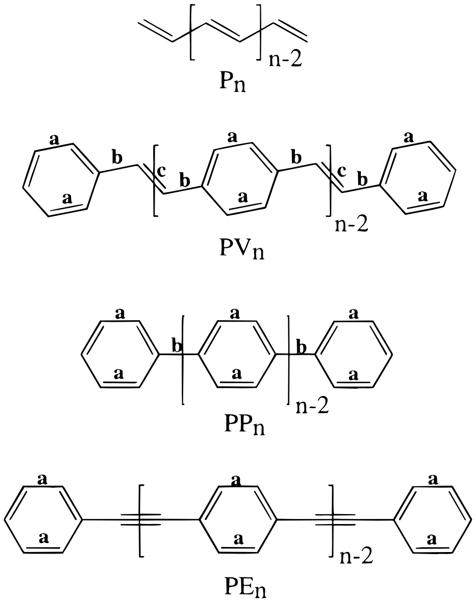
SCHEME 1



correlation is more important for the lowest even-parity excitons than for the odd-parity ones, but the same applies to the excited-state structural changes. Polyenes (P_n), which can be viewed as prototypes for the majority of conjugated systems, are the best example.[22] Therein 1^1B_u diminishes the bond alternation inherent to the ground state, whereas 2^1A_g reverts it, rendering ground-state single bonds shorter than the ground-state double bonds.[23] Yet the adiabatic description of the lowest ^1B_u and ^1A_g excitons has led us to the conclusion that a crossover to an even-parity S_1 takes place in long oligorylenes,[24] in agreement with the drop of luminescence.[25] Although this is not the case for PPP, PPV and PPE and their oligomers studied herein, we feel that understanding of two-photon and higher processes in these systems would be incomplete without an adiabatic picture of the relevant excited states.

2. Methods

Between the two most recent semiempirical methods of the MNDO family, AM1[26] and PM3,[27] preference was given to the former because of the more realistic results it provides for the torsional displacement of benzene rings in biphenyl (PP_2) and *trans*-stilbene (PV_2) (see Scheme 1 for denotations). The PM3 approach predicts a planar structure for both. Whereas for *trans*-stilbene this result[28] compares well with X-ray data and fluorescence studies, a planar ground-state conformation of biphenyl is definitely not acceptable. AM1 predicts ~45° twisted phenyl rings in biphenyl, and a ~16° torsional angle ϕ around the single bonds **b** in *trans*-stilbene. For both molecules, these results are in good agreement with high-level ab initio studies.[29−31] Still, it should be born in mind that the ring-torsional potential in *trans*-stilbene is very flat around the equilibrium, and the energy barrier at $\phi \sim 0°$ may be vanishingly small.[29,30] As discussed further, if CI is extended within the AM1 model, a nearly planar ground-state conformation of *trans*-stilbene is predicted.

Whereas the AM1 model is deemed to provide realistic molecular geometries and potential energies, it does not belong to the methods adapted for spectroscopic purposes. Brédas and co-workers[15] have used the spectroscopy-oriented INDO method to assess transition energies in oligo(*p*-phenylenevinylenes), pre-optimized by means of AM1. Herein we focus on the adiabatic description of excited states, which reflects the changes in structure relative to the ground state. Hence, it is a matter of consistency to treat electronic and nuclear degrees of freedom within one and the same model. Therefore, reported excitation energies pertain to the same AM1-based approach, which we used to locate and assess the potential energy equilibria in the ground and excited states. In view of the detailed spectroscopic[4] and theoretical[22] description of polyenes, they are addressed in this paper mainly with the purpose to benchmark the accuracy of the computational approach chosen. The likely limitations of the AM1 Hamiltonian in the assessment of transition energies in conjugated systems with aromatic rings are highlighted herein on the example of benzene. Table 1 compares the AM1 excitation energies for the three lowest singlet $\pi-\pi^*$ transitions in benzene with experimental data and high-level ab initio results.[32] Computations were performed with minimal CI, involving the four frontier π-orbitals of benzene under D_{6h}. Whereas accurate quantum-chemical methods provide energies within ~0.15 eV from experiment, the AM1 description is only qualitative. The $\pi-\pi^*$ transition energies are substantially underestimated. The most notable disagreement is for the 1^1B_{1u} state, where the AM1 result is lower in energy by over 1 eV. For the lowest excited 1^1B_{2u} state and the dipole-allowed 1^1E_{1u} ones, the discrepancies are around 0.5 and 0.6 eV, respectively. The disagreement of the AM1 results is to be attributed mainly to the semiempirical Hamiltonian since extension of the CI active space does not lead to improvement.

TABLE 1: Computed and Experimental $\pi-\pi^*$ Excitation Energies (eV) of Benzene

symmetry	AM1	CCSD(T)[a]	expt[a]
B_{2u}	4.48	4.74	4.90
B_{1u}	4.98	6.17	6.20
E_{1u}	6.30	6.99	6.94

[a] Coupled-cluster ab initio and experimental vertical excitation energies from ref 32.

For the computation of excited states MOPAC[33] has been extended[24] to work for a spin- and symmetry-adapted CI basis and to handle CI up to the complete active space of 10 electrons in 10 MOs (CAS[10,10]) without contraction of the wave function. Geometry optimization with CI above CAS[6,6] was performed, however, in a contracted CI basis restricted to the dominant configurations. As a criterion the norm of the projection of the wave function onto the contracted CI basis was used. The lowest threshold set was 0.99 for CAS[10,10] optimizations. Finally, equilibrium point computations were performed without contraction. To avoid size-consistency problems, computations were performed at CAS level, by keeping the size of the active space proportional to the number of repeat units in the oligomers. Thus, the molecules with $n = 2$ phenyl rings were treated in minimal basis (HOMO and LUMO), and a pair of occupied and virtual orbitals was added to the active space for each repeat unit more, up to CAS[10,10] for $n = 6$.

Extended 1,4-phenylene bridged systems with n benzene rings have n bonding and n antibonding near-degenerate π-orbitals[8] that are localized exclusively on bonds **a** of the phenyl/phenylene rings. Their energies fall into the valence and conduction bands of the corresponding polymers. In PP_n and PE_n, the CI active space of $2n - 2$ MOs specified thus reaches these localized π-levels for $n > 2$. Within AM1, this limit is reached above $n = 6$ for PV_n. Since these orbitals are disjoint and extraneous to π-conjugation between repeat units, they were excluded from the CI active space by an automatic selection, which admits only MOs of the same symmetry as the frontier ones. Thus,

TABLE 2: Calculated and Experimental Excitation Energies (eV) of Polyenes with *n* Double Bonds

n	$1B_u$ vert	$1B_u$ adiab	$1B_u$ obsvd[b]	$2A_g$ vert	$2A_g$ adiab	$2A_g$ obsvd[c]
3			4.5			4.223
4 (5)[a]	4.01	3.86	3.98 (3.62)	4.07	3.34	3.557 (3.032)
6 (7)	3.42	3.24	3.34 (3.13)	3.32	2.52	2.699
8 (9)	3.07	2.88	2.96 (2.83)	2.92	2.09	2.217 (2.422)
10 (11)	2.87	2.66	2.72 (2.64)	2.72	1.82	

[a] Values in brackets for polyenes for which no calculations were done. [b] 0−0 $1B_u \leftarrow 1A_g$ transitions of *tert*-butyl capped polyenes from ref 37. [c] Reference 22 and references therein.

computations were performed for a CI active space encompassing all extended π-orbitals, which pertain to the valence and conduction bands of the polymer. Structure optimization was performed for all internal degrees of freedom under symmetry restraints reflecting the corresponding point group adopted.

In the further use is made of the well-known empirical rule associating excitation energies of oligomers with the reciprocal conjugation length, $1/n$,

$$E_n = E_\infty + A/n \tag{1}$$

where E_∞ is supposed to reflect the excitation energy of the corresponding extended polymer. The rule has been seriously questioned as the most suitable approximation (and extrapolation) of the longest-wavelength absorption peaks of ring-containing conjugated systems in particular.[34] We point out in advance that for this particular case neither adiabatic, nor vertical excitation energies should be expected to correspond to the spectral maxima. Oligo(*p*-phenylenevinylenes), for instance, exhibit pronounced vibronic progressions in absorption and emission as a result of at least two coupled bond-stretching modes.[35,36] The apparent 0−0 vibrational feature does not survive as the most intensive peak in absorption.[35] The *E* vs $1/n$ plots are essential insofar as they permit a better comparison of the way in which excited states and relaxation energies evolve with increasing *n* for different conjugated systems.

3. Results and Discussion

Polyenes. All-trans even polyenes P_n of C_{2h} symmetry for $n = 4$, 6, 8, and 10 double bonds were optimized in their ground ($1A_g$), odd-parity ($1B_u$) and even-parity ($2A_g$) excited states (the spin index for singlet is omitted hereafter). The CI active space was set equal to the number of double bonds and encompassed thus the half of the π-electrons. The results are summarized in Table 2, together with observed excitation energies taken from the literature.[22,37] Figure 1 is a plot of excitation energies versus reciprocal chain length, $1/n$. The results for the adiabatic $1B_u$ state are in very good agreement with the 0−0 transition energies of *tert*-butyl capped polyenes.[37] Similarly, the energy of the $2A_g$ state is reproduced fairly well, albeit its adiabatic energy is systematically underestimated. Relaxation energies, expressing the difference between computed vertical and adiabatic transitions, are assessed at less than 0.2 eV for $1B_u$, and do not increase substantially with n. The $2A_g$ state is associated with much stronger structural relaxation which comes close to 1 eV in P_{10} and should become equal to the Peierls band-gap when *n* approaches infinity.

Oligo(*p*-phenylenevinylenes). Depending on the rotational directions, equivalent torsions around the two symmetric single bonds **b** in *trans*-stilbene lead either to C_2 or S_2 (C_i) nonplanar conformations. Although the former has been found slightly more stable with AM1 and ab initio methods,[29,30] we have adopted model geometries with inversion center to preserve strict selection-rule differentiation of excited states. With regard to the 1,4-phenylene axis, the torsions of the two adjacent **b**-bonds were also taken with opposite directions of rotation, leading to a linear structure with alternating ring rotations in larger oligomers.

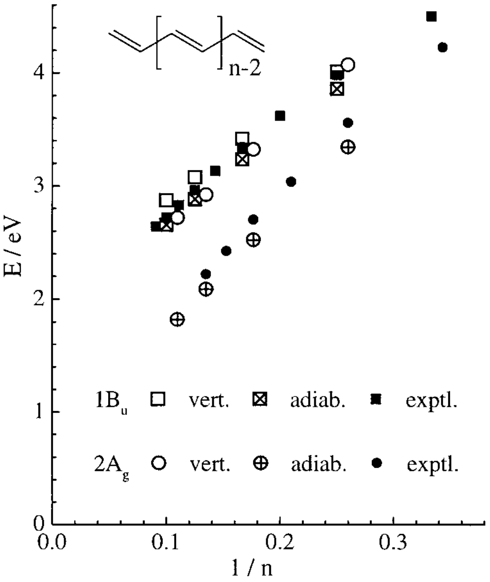


Figure 1. Calculated and experimental[22,37] excitation energies of P_n as a function of $1/n$. Tags for $2A_g$ are slightly offset along the reciprocal chain-length axis to prevent overlap.

The lowest excitations in *p*-phenylene-based oligomers involve mainly HOMO and LUMO. Within the manifold of two-photon excited states, only the one bearing a relation to $2A_g$ in polyenes was studied in more detail. Its dominant configuration is a double excitation from HOMO to LUMO. Because of its doubly excited character, relaxations in direction to the quinoid structure are more considerable than for the HOMO → LUMO singly excited odd-parity state. Within the CI scheme adopted, this two-photon state was obtained as $3A_g$ at ground-state equilibrium for all oligomers except stilbene. However, it becomes the lowest dipole-forbidden excited state in the adiabatic description. For stilbene and *p*-distyrylbenzene the two-photon excited state in question required special consideration. In minimal CI, the $2A_g$ state of centrosymmetric stilbene is associated with occupation numbers close to 2 for the LUMO and close to 0 for the HOMO. The double-bond localization of the linear inter-phenyl linkage is reverted, so that the two **b**-bonds acquire more double-bond character and become less susceptible to torsion than the central **c**-bond. The relaxed $2A_g$ structure is practically planar (C_{2h}) but is a saddle point on the excited-state potential energy surface with regard to a_u distortions involving rotation around bond **c**. Under C_2 where inversion symmetry is removed, the doubly excited state (former $2A_g$) approaches the *cis*-isomer, being correlated with the ground electronic state of the latter. When CI is increased, however, the $2A_g$ state of *trans*-stilbene appears to be stabilized with respect to torsion around **c** (see Figure 6 further). The doubly excited state of PV_3 was also checked against such instabilities at the CAS[4,4] level adopted for the trimers. In fact, simultaneous antiparallel torsions around the two **c**-bonds in PV_3 comply to S_2 symmetry but are unfavorable for the $2A_g$ state. The two-photon exciton relaxes into a C_2 structure with **c**-bonds rotated at ∼49° each. The adiabatic energies for the 2A excited state in PV_2 and PV_3 of C_2 symmetry are given in Table 3, in parallel to those for centrosymmetric phenylenevinylenes. The

TABLE 3: Calculated Excitation Energies and S_0-S_1 Absorption and Emission Peaks (eV) of Oligo(*p*-phenylenevinylenes) with *n* Rings

n	$1B_u$ vert	$1B_u$ adiab	absorption[a] (emission)[b]	$2A_g$ vert	$2A_g$ (2A) adiab
2	4.08	3.72	4.01 (3.70)	7.22	5.58 (3.95)
3	3.61	3.27	3.44 (3.20)	4.97	3.82 (3.80)
4	3.34	3.02	3.20 (2.85)	4.53	3.60
5	3.18	2.89	3.07 (2.75)	4.32	3.46
6	3.07	2.82	3.01	4.18	3.41
7			2.96		

[a] Absorption maxima of *tert*-butyl capped PV_n from ref 38. [b] 0−0 photoluminescence peaks of *tert*-butyl capped PV_n from ref 36.

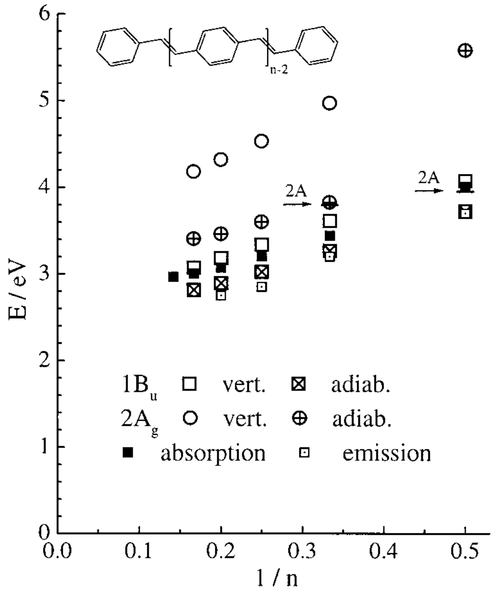


Figure 2. Calculated excitation energies and positions of absorption[38] and photoluminescence[36] peaks of PV_n.

TABLE 4: Calculated Excitation Energies and S_0-S_1 Absorption and Emission Maxima (eV) from Reference 40 of Oligo(*p*-phenylenes) with *n* Rings

n	$1B_1/1A_u$[a] vert	$1B_1/1A_u$ adiab	absorption (emission)	$2A/2A_g$ vert	$2A/2A_g$ adiab
2	4.57	4.19	4.92 (3.94)	8.12	6.52
3	4.08	3.72	4.34 (3.64)	5.49	4.47
4	3.82	3.46	4.11 (3.36)	5.06	4.12
5	3.66	3.32	3.98 (3.30)	4.85	3.96
6	3.56	3.23	3.91 (3.27)	4.73	3.87

[a] Even/odd number of rings.

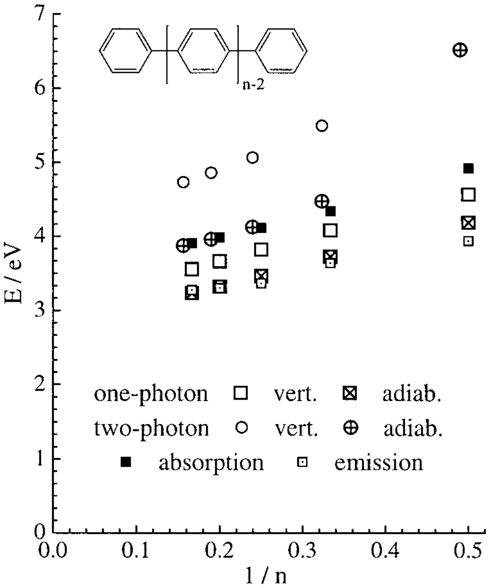


Figure 3. Calculated excitation energies and absorption and emission maxima[40] of PP_n. Tags for the two-photon states are slightly offset.

two-photon exciton in the tetramer was found to produce a planar structure. Being sufficiently delocalized, it implies a lack of significant bond alternation in the inter-ring bridges, and hence was found stable against noncentrosymmetric distortions.

The calculated excitation energies for PV_n are summarized in Table 3, together with the absorption maxima[38] and the characteristic peaks in photoluminescence[36] for comparison. As seen from Figure 2, the absorption peaks assigned to the 1−0 vibrational harmonics in bond-stretching modes[35] are slightly higher than the calculated adiabatic excitation energies, and slightly lower than the vertical ones. The emission maxima, which correspond to the 0−0 vibrational feature,[36] are also close to the $1B_u$ adiabatic excitation energies. The $2A_g$ state approaches $1B_u$ very slowly with increasing conjugation length. Two-photon absorption studies[39] position $2A_g$ around 0.5 eV above the optical band gap in the polymer. Our estimate is 0.59 eV for the adiabatic gap between the odd- and even-parity excitons in PV_6. Relaxation energies of the former decrease from 0.37 to 0.25 eV on going from *trans*-stilbene to PV_6, in parallel with a decrease of the relative structural changes in the excited state. The extrapolation linear in 1/n leads to even lower estimate of the electron−lattice relaxation for the exciton−polaron in the polymer. The relaxation energies of the even-parity exciton are significantly larger. The estimated value is 0.77 eV for PV_6, but still much less than the one in polyenes of comparable conjugation length.

Oligo(*p*-phenylenes). Oligo(*p*-phenylenes) with *n* phenyl/phenylene rings (PP_n) were adopted to be of D_2 and C_{2h} point groups for even and odd *n*, respectively. As for oligo(*p*-phenylenevinylenes), the model geometry of PP_n assumed an alternating ring-rotational motif. Again, two-photon states other than the one with leading double excitations are not considered in details, albeit obtained in the calculations. To circumvent the need to use different labeling of excited states in different oligomers, we will denote the dipole-allowed exciton by 1B and the dipole-forbidden one by 2A, bearing in mind that the latter is obtained as $3A_g$ or 3A for $n > 2$ at ground-state geometries. Still it becomes the lowest two-photon excited state when structural relaxations are taken into account.

In comparison to PV_n, π-conjugation of *p*-phenylenes is worsened by more pronounced effective bond alternation[8] and significant ring torsions, which persist in the excited states. Relative structural changes upon excitation are largest in biphenyl and decrease in longer PP_n where excitons can delocalize. Nevertheless, biphenyl is not planar in S_1. Planar structures are predicted for 2A up to the trimer. For larger oligomers terminal rings are rotated out of plane even in the doubly excited state, although the latter induces more substantial quinoid distortions than the dipole-allowed one. The gap between 1B and 2A again decreases with *n* down to 0.64 eV in PP_6 (see Table 4 and Figure 3). Similarly, differences between vertical and adiabatic excitation energies are larger than for PV_n, although the *p*-phenylene topology is less susceptible to changes in bond alternation. This can be ascribed to the fact that ring rotations are much more involved in excited-state relaxations of PP_n. Still, relaxation energies of 1B are too small to explain

TABLE 5: Calculated Excitation Energies (eV) for Oligo(*p*-phenylenethynylenes) with *n* Rings

n	$1B_{1u}$ vert (adiab)	$2A_g$ vert (adiab)	$3A_g$ vert (adiab)
2	4.41 (4.14)		7.98 (6.64)
3	3.85 (3.63)	4.96 (4.79)	5.37 (4.70)
4	3.58 (3.40)	4.38 (4.27)	4.94 (4.45)
5	3.44 (3.27)	4.05 (3.93)	4.75 (4.25)
6	3.35 (3.20)	3.83 (3.72)	4.65 (4.17)

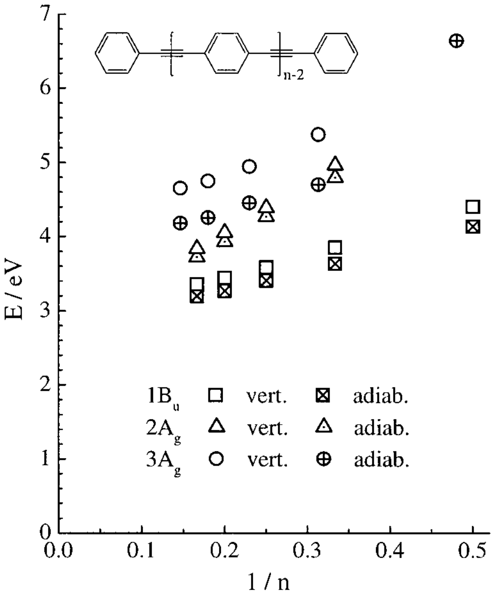


Figure 4. Calculated excitation energies of PE_n. Tags for $3A_g$ are slightly offset.

the presence of even larger Stokes' shifts. Absorption maxima[40,41] are observed above the computed vertical 1B ← 1A transition energies.

Oligo(*p*-phenyleneethynylenes). The conjugated backbone of *p*-phenyleneethynylenes is similar to that of PV's, except for the presence of a triple bond in the inter-ring bridge instead of a double one. The shorter triple bond produces stronger bond alternation, which increases the intrinsic band gap and is unfavorable for conjugation, but warrants a rigid-rod structure. Ring rotations in the ground state are very facile and practically do not couple to delocalized π-electrons. The orthogonal 2p orbitals at the triple bonds provide inter-ring π-conjugation almost independent of torsion. PPE and PE_n have been typically synthesized[42,43] with alkyl ether or alkyl ester side chains at 2,5-phenylene positions. Their alignment in the solid state provides a nearly planar conformation of the conjugated backbone.[43] Therefore, planar PE_n's of D_{2h} symmetry were taken as models. The results obtained for the lowest odd-parity exciton and the first two dipole-forbidden excited states are given in Table 5 and Figure 4. In contrast to PV_n and PP_n, the lowest even-parity exciton in PE is not the one typical for polyenes. Apparently, reversion of bond alternation toward the quinoid form is strongly impeded by the triple bonds. The HOMO−LUMO doubly excited state appears now as $3A_g$ for the longer oligomers even in the adiabatic description, although it is associated with more pronounced structural changes. The $2A_g$ state is dominated by HOMO → LUMO + 1 and HOMO-1 → LUMO single excitations, and therefore its relaxation energy is relatively small. As a matter of fact, the A_g singly excited state is slightly higher than the doubly excited one in PE_3, so that the $2A_g$ denotation is formally incorrect in this case, but the former drops faster in energy for longer oligomers than the latter. $S_0 \rightarrow S_1$ transition energies are obtained ~0.4 eV higher than those of PV_n with the same number of benzene rings. They are lower than those of PP_n, but PE_n correspond to larger conjugation lengths because of the two bonds more per repeat unit. The vertical $1B_{1u} \leftarrow 1A_g$ transition energies give a value of around 2.8 eV for the optical band gap when extrapolated to the polymer. PPE with $OC_{12}H_{25}$ side chains has absorption maxima at 3.0 eV in solution and 2.74 eV in the solid state.[44] In line with the expected weaker electron−lattice coupling in PE_n, relaxation energies are much smaller than for PV_n and PP_n. The relaxation energy for the odd-parity exciton is estimated to decrease from 0.27 eV in diphenylacetylene to 0.15 eV in PE_6. The lack of ring-rotational displacement between ground and excited states leads to Stokes' shifts of around 0.35 eV for the trimer and 0.19 eV for the polymer with alkoxy side chains.[45]

Figure 5 is a scheme for the distribution of the excitation

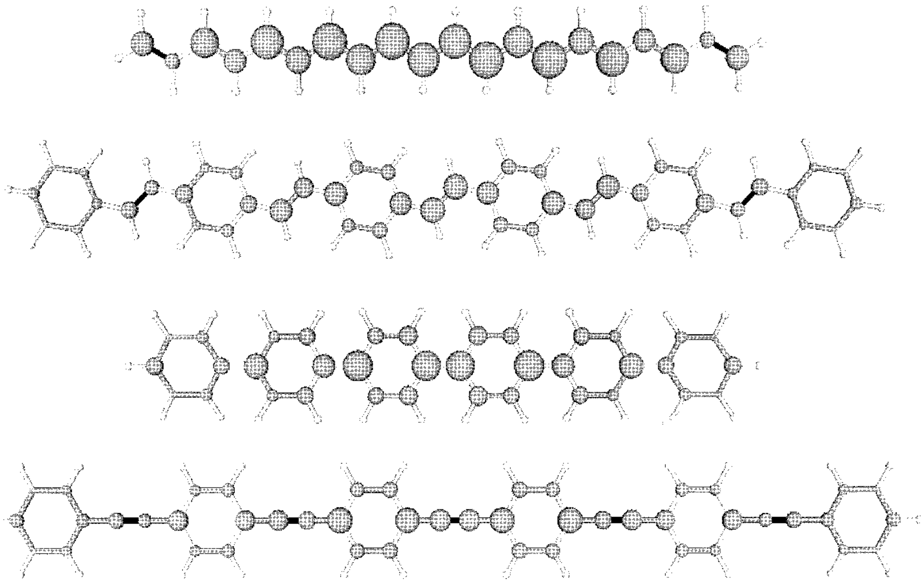


Figure 5. Excitation amplitudes and structure of the adiabatic one-photon excited states in P_{10}, PV_6, PP_6 and PE_6. Excitation amplitudes are given by the diagonal elements of CI density matrix in electron−hole representation. CC bonds lengths larger than 1.41 Å are in light gray; within 1.36−1.41 Å, in dark gray; shorter than 1.36 Å, in black.

amplitudes over π-sites for the one-photon excited states in the longest oligomers considered. The $1B_u$ exciton in P_{10} can be viewed as a predecessor of the relaxed odd-parity excited state in PA. The latter is deemed to extend infinitely as a pair of oppositely charged solitons if electron−hole attraction is neglected.[46] From Figure 5 it can be inferred that like for P_{10}, the excitons in PV_6, PP_6 and PE_6 are still confined by finite oligomeric length, rather than by self-trapping. Apparently, the intrinsic exciton−polaron length is not yet reached in conjugated segments involving six benzene rings for any of the phenylene-based systems addressed. Excitation amplitudes decrease, but do not disappear on the terminal phenyl rings suggesting a further delocalization of the excited state in an extended polymer. In comparing of the predicted structures of the excitons in the different ring-containing systems, it should be born in mind that the largest excitation amplitudes reside on the vinylene units for PV and on the bridgehead phenyl/phenylene sites for PP and PE. Therefore, the slightly larger excitation amplitudes at the terminal *p*-phenyl sites in PP_6 and PE_6 do not imply that the exciton−polarons in PPP or PPE should be more extended than in PPV.

Effect of Electron Correlation and Ring-Torsional Potential. Excited states decrease, remove or even invert the bond alternation, which is induced by the highest bonding orbitals occupied in the ground state. Therewith, a more planar excited-state structure with a quinoid contribution is stabilized in ring-containing conjugated systems such as those studied. Thus, the structural distortions in the excited state have two major components: the first is in CC bond lengths, and the second, in ring torsions. Whereas the former can be easily recognized by the vibronic progressions in spectra, ring rotations and other low-frequency modes cannot be resolved, but may contribute to Stokes' shifts.[36,47]

From a theoretical perspective it has been shown[48] that electron correlation reduces bond alternation in conjugated system. Hence, results obtained without or with limited CI are naturally expected to overestimate double-bond localization both in the ground and excited states and, therewith, the structural difference between them. To assess the effect of electron correlation, and the limitations arising from the inevitable restriction of CI, the molecules with two phenyl rings were taken as models. We concentrated on the ring-rotational potential since its profile practically reflects the π-component of the bond(s) rotated. Since the relative position of the electronic states is not an issue in this case, CI with all singles and doubles (CISD) for the complete π-electronic space was employed. The results are illustrated in Figure 6, together with those obtained from minimal CI for comparison. For stilbene the two **b**-bonds were rotated parallel under C_2 or antiparallel under S_2. In the two-photon excited state (2A under C_2) the rotation is around the central bond **c** since this bond becomes more susceptible to torsion. The difference in ground-state torsional potential illustrates the importance of electron correlation. Configuration interaction suggests a more balanced distribution of π-density over the inter-phenyl linkage, which stiffens the two **b**-bonds and renders the structure planar. Minimal CI overestimates changes in bond alternation for the dipole-allowed exciton. It predicts a steeper torsional potential around **b**-bonds that now acquire more aromatic character than in the ground state. The collapse of the two-photon excitation into a cisoid structure, predicted with minimal CI, is due to the reversal of the bond alternation in the inter-ring bridging unit. The 2A torsion potential for bond **c** is rather flat when π-correlations are better accounted for. In line with the notion that electron−lattice

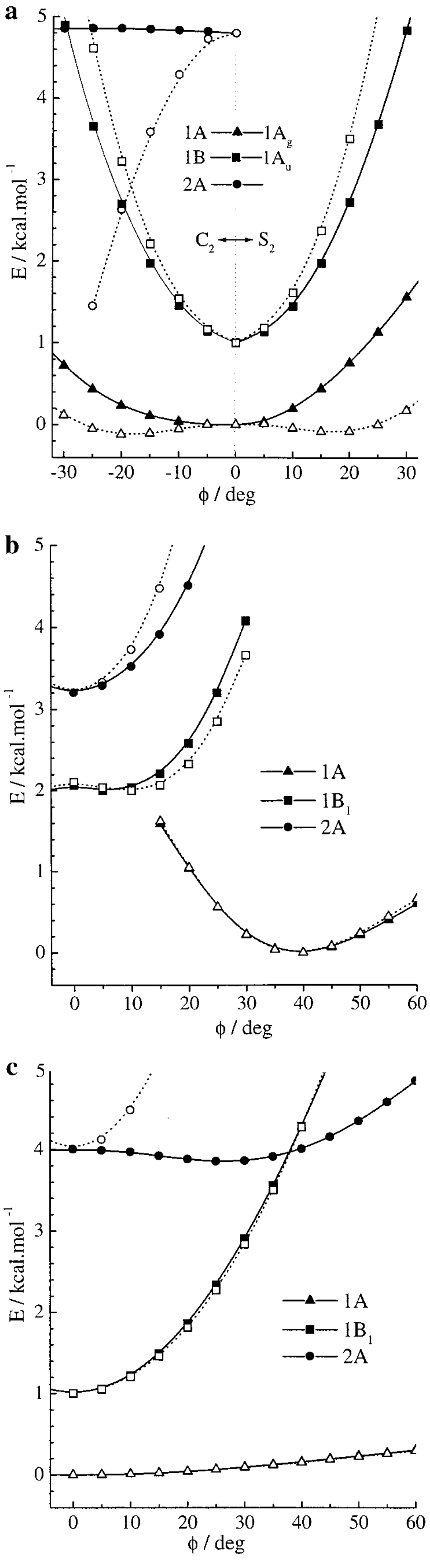


Figure 6. Ring-torsional potential of (a) *trans*-stilbene, (b) biphenyl, and (c) diphenylacetylene: (solid curves) result from CISD for all π-electrons; (dotted curves) minimal CI. For *trans*-stilbene rotation is around the two **b**-bonds for the ground and one-photon excited states and around the **c**-bond for the two-photon excited state. The offset of the electronic origins is arbitrary.

coupling is weaker in *p*-phenylenes and *p*-phenyleneethynylenes, ground- and excited-state torsional potentials are not much influenced by electron correlation. The curves obtained with minimal and extended CI are rather close. The largest ring-rotational displacement in excited states is predicted for biphenyl. The ethynylene bridge in diphenylacetylene allows almost free ring rotation in the ground state, but a coplanar structure is slightly stabilized in the lowest excited one. Extended CI suggests that the equilibrium of the even-parity exciton is moved by around 20° from coplanarity.

4. Conclusions

The computations performed position the two-photon excited states in phenylene-based conjugated systems above the lowest, strongly dipole-allowed transition, which is dominated by the HOMO → LUMO single excitation. In the adiabatic approximation, the lowest even-parity excited state in *p*-phenylenevinylenes and *p*-phenylenes is predicted to be of the same nature as 2^1A_g in polyenes. Being dominated by the double HOMO → LUMO excitation, it involves more pronounced structural changes than the lowest one-photon exciton. However, when comparison with the results for polyenes is made, relaxation energies are generally smaller and tend to decrease with oligomeric length as a natural consequence of the presence of aromatic rings in the conjugated backbone. In *p*-phenyleneethynylenes, a singly excited dipole-forbidden singlet approaches the dipole-allowed state faster than the HOMO → LUMO double excitation, but is predicted to remain above the optical threshold up to the oligomer with six benzene rings.

Computed relaxation energies for the lowest one-photon states are compared with the Stokes' shifts, observed in photoluminescence. The difference between the vertical and adiabatic transition energies is obtained to decrease from *p*-phenylenes to *p*-phenylenevinylenes, to *p*-phenyleneethynylenes. This is in line with the different magnitudes of the Stokes' shifts in these systems. Although the *p*-phenylene skeleton is less predisposed to quinoid distortions in bond alternation than PPV, the largest differences between vertical and adiabatic excitation energies are obtained particularly in this case. This result can be attributed to the presence of larger inter-ring torsions in ground-state *p*-phenylenes, which are significantly suppressed in the excited states. Correspondingly, excited-state relaxations in ring-torsional degrees of freedom are predicted to be more pronounced than in *p*-phenylenevinylenes, where both the ground- and excited-states conformations are very close to planarity. The triple bond in *p*-phenyleneethynylenes makes π-conjugation between benzene rings nearly independent of ring torsions and almost eliminates ring-torsional preferences.

For *p*-phenylenevinylenes and *p*-phenylenes, computed lowest excitation energies evolve with reciprocal conjugation length nearly parallel to the absorption and emission peaks. Despite the satisfactory agreement between adiabatic transition energies and the positions of the primary photoluminescence peaks, the results give no accurate quantitative assessment of Stokes' shifts, especially for PP_n. In continuation of this study, the line shapes of the lowest one-photon transitions in absorption and emission have been calculated in Condon approximation from the computed distortions and totally symmetric normal modes. The preliminary analysis suggests that important features of spectra like Stokes' shifts and spectral broadening can be explained only when vibrational coupling, including ring-torsional modes, is taken into account explicitly.

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