Energetics and electronic structure of phenyl-disubstituted polyacetylene: A first-principles study

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Phenyl-disubstituted polyacetylene (PDPA) is an organic semiconductor which has been studied during recent years for its efficient photoluminescence. In contrast, the molecular geometry, providing the basis for the electronic and optical properties has been hardly investigated. In this paper, we apply a density-functional-theory based molecular-dynamics approach to reveal the molecular structure of PDPA in detail. We find that oligomers of this material are limited in length, being stable only up to eight repeat units, while the polymer is energetically unfavorable. These facts, which are in excellent agreement with experimental findings, are explained through a detailed analysis of the bond lengths. A consequence of the latter is the appearance of pronounced torsion angles of the phenyl rings with respect to the plane of the polyene backbone, ranging from 55° up to 95°. We point out that such large torsion angles do not destroy the conjugation of the π electrons from the backbone to the side phenyl rings, as is evident from the electronic charge density.

I. INTRODUCTION

In the emerging field of nanotechnology conjugated polymers are playing an important role as materials of choice for organic light emitting diodes (OLEDs),[1,2] organic field effect transistors (OFETs),[3] organic lasers,[4,5] photocells,[6] etc. Their application in such devices requires the search and the investigation of new materials with interesting optical and electronic properties. PA which is the simplest and the most widely studied conjugated polymer, exhibits very weak photoluminescence[1,7,8] (PL), thus ruling it out as a candidate for opto-electronic applications. However, in the last decade, phenyl-disubstituted polyacetylene (PDPA) derivatives, obtained by replacing hydrogen atoms of *trans*-polyacetylene (PA) by phenyl rings or their derivatives, were demonstrated as luminescent materials with high quantum efficiency, which also exhibited stimulated emission in thin film form.[9,10] Therefore, one anticipates that they will be useful in creating light emitting diodes and polymeric lasers.[11]

To understand the physics behind the fluorescence of these materials, a series of experimental and theoretical investigations have been performed.[10–22] From calculations based on a Pariser-Parr-Pople (PPP) model Hamiltonian it was argued that this phenomenon is due to reverse excited-state ordering (compared to PA) of the one-photon allowed $1B_u$ and two-photon allowed $2A_g$ states, caused by reduced electron correlation effects due to the presence of phenyl rings.[11,16,17] In PA, the $2A_g$ state occurs below the $1B_u$ level, as a consequence of which the optically pumped $1B_u$ state decays rapidly to the $2A_g$ state, and according to dipole transition rules, radiative transition between $2A_g$ and the $1A_g$ states is forbidden. Hence it was concluded that in contrast to PA, PDPA shows strong PL as $E(2A_g) > E(1B_u)$, where $1B_u$ is strongly dipole coupled to the ground state.

While most of the investigations concentrated on the optical properties of PDPAs their structural properties have hardly been investigated. A complete understanding of the electronic and hence optical properties is, however, impossible without knowing the respective ground state geom-

etries. This leads to another puzzling issue, namely, the reason behind the experimentally observed short conjugation length of these materials, which typically consist of seven repeat units in PDPA thin films,[12] and only five in solution.[23] Based upon an SSH model calculations, it was predicted in an earlier work that for an infinite chain, introduction of phenyl rings will lead to a reduction of bond alternation along the backbone.[11]

The aim of this work is to throw light on the formation of PDPAs by investigating their energetics as a function of oligomer length. To this extent we carry out first-principles calculations based on density-functional theory (DFT). We thereby focus on the geometry, including a detailed study of bond lengths and alternations, as well as the orientation of the phenyl rings with respect to the polyene backbone. We will show that polymerization of PDPAs is hampered by single-bond breaking, and oligomers are only stable up to eight repeat units. Moreover, an analysis of band gaps and charge densities allows for an insight into the lowest optical transitions.

II. PDPA AND ITS OLIGOMERS

The crystal structure of PA is of herringbone type, where the polymer chains are coupled by the weak van der Waals interactions. Although the three-dimensional (3D) environment can have a large impact on the optical properties on such systems,[24,25] it can be considered as quasi-one-dimensional for the current investigation, where we study the cohesive properties as a function of chain length. Hence we model PA, and consequently PDPA, as strictly one-dimensional zigzag chains.

The PDPAs with the formula unit $C_{14}H_{10}$ are obtained by replacing the hydrogen atoms of PA (C_2H_2) by phenyl groups, leading to the structure presented in Fig. 1. The backbone polyene chain is running along the x axis (longitudinal direction) while the phenyl rings are oriented along the y axis (transverse direction). The single and double bonds are labeled as r_s and r_d, respectively, while the bond alternation
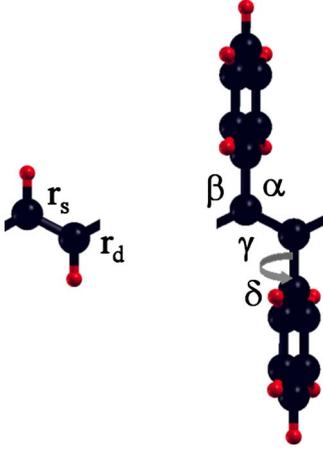
FIG. 1. (Color online) Repeat units of polyacetylene and phenyl-disubstituted polyacetylene. Large and small spheres denote carbon and hydrogen atoms, and r_s and r_d represent single and double bond lengths, respectively.

is defined as $\Delta r = r_s - r_d$. α and β denote the angles between the carbon atoms of the backbone and the phenyl ring, γ is the angle between the carbon atoms of the backbone, and δ is the torsion angle of the phenyl ring with respect to the backbone plane. The PDPA oligomers are terminated with one hydrogen atom at either end, saturating the dangling bonds. The formula units of PDPAs and PAs are $C_{14n}H_{10n+2}$ and $C_{2n}H_{2n+2}$, respectively, with n being a positive integer representing the number of repeat units. We adopt the notation PDPA-n, and correspondingly PA-n for the oligomers of PA.

III. COMPUTATIONAL DETAILS

In the present work, infinite PDPA as well as its oligomers with two to six building blocks are investigated by means of density-functional theory employing the supercell approach. A vacuum region of around 8 Å is adopted along the y and z directions for the polymers, and also in the third dimension for the oligomers. This size is considered sufficient to avoid interaction between the translational images. All the geometries are optimized, where we assume the structures to be relaxed when the forces on individual atoms are below 1 meV/Å. To this extent, the projector augmented wave (PAW) method is utilized as implemented in the original PAW code.[26] It makes use of Car-Parinello molecular dynamics allowing for geometry optimization in an accurate and efficient manner. Polynomial-type pseudopotentials as implemented in the code are used, with a plane wave cutoff of 30 Ry. A Brillouin zone sampling of $16 \times 1 \times 1$ **k** points is taken for the calculations of polymers, while the finite systems naturally requires one **k** point only. Exchange-correlation effects are treated by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) flavor.[27] We further discuss the issue of our choice of the exchange-correlation functional at the end of Sec. IV A.

The polymerization energy E_{poly} is calculated using the formula

$$E_{poly} = E_{polymer} - E_{monomer}, \qquad (1)$$

where $E_{polymer}$ is the total energy per unit cell of the infinite polymer and $E_{monomer}$ is that of diphenyl acetylene, $C_{14}H_{10}$,
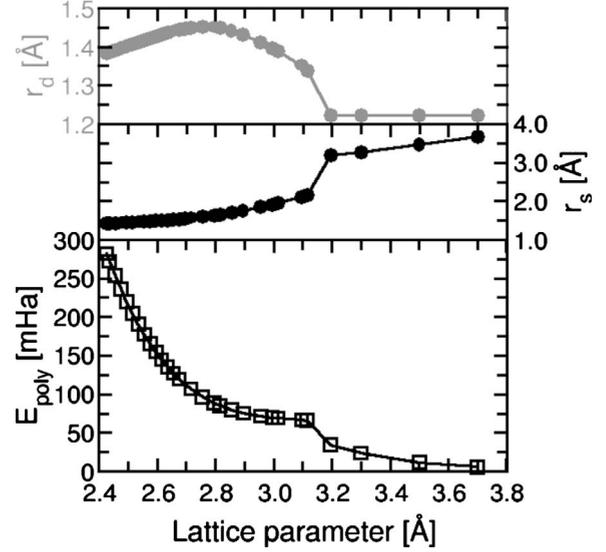

FIG. 2. Variation of the single bond length, r_s, double bond length, r_d, (top) and polymerization energy, E_{poly}, of infinite PDPA (bottom) as a function of the lattice parameter a.

in its optimized geometry. The choice of $C_{14}H_{10}$ as the monomer is based upon the fact that it has the same chemical formula as of the repeat unit shown in Fig. 1. Moreover, in experimental situation also PDPA derivatives are usually synthesized using diphenyl acetylene monomer and the $TaCl_5$-Bu_4Sn catalyst.[23] Therefore, we believe that our choice of using diphenyl acetylene as a monomer is on a strong footing from a chemical point of view.

Similarly, we define an oligomerization energy, E_{oligo}, as

$$E_{oligo} = \frac{1}{n}(E_{oligomer} - nE_{monomer} - 2E_H), \qquad (2)$$

where $E_{oligomer}$ is the total energy of the respective oligomer and E_H is that of the hydrogen atom.

IV. RESULTS

A. Structural properties

To evaluate the stability of PDPA we calculate the polymerization energy as a function of the lattice parameter a, which is displayed in Fig. 2 (bottom panel). The most striking result is that the values are positive over the whole range, indicating that the system is not bound at all. The energy monotonically decreases with increasing lattice parameter up to $a \approx 3.1$ Å followed by a double kink which is explained by a change in the bonding characteristics. On analyzing the single and double bond lengths (top panel) we see that first both of them increase due to steric hindrance between the phenyl rings, until the double bond reaches a value of ≈ 1.45 Å. With even larger lattice spacing, the single bond length keeps increasing while the double bond length goes down, because any further increase would correspond to a single bond, which is impossible given the chemical structure. Once a reaches 3.115 Å, r_d becomes smaller than 1.34 Å, while r_s gets larger than 1.54 Å, values typical for
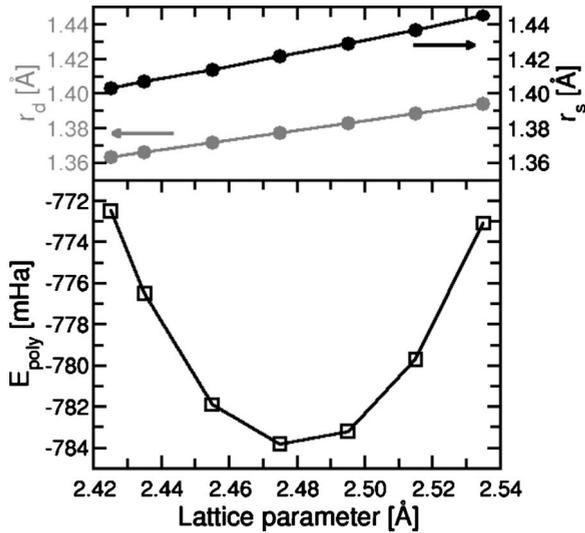
FIG. 3. Variation of the single bond length, r_s, double bond length, r_d, (top) and polymerization energy, E_{poly}, of polyacetylene, as a function of the lattice parameter a.
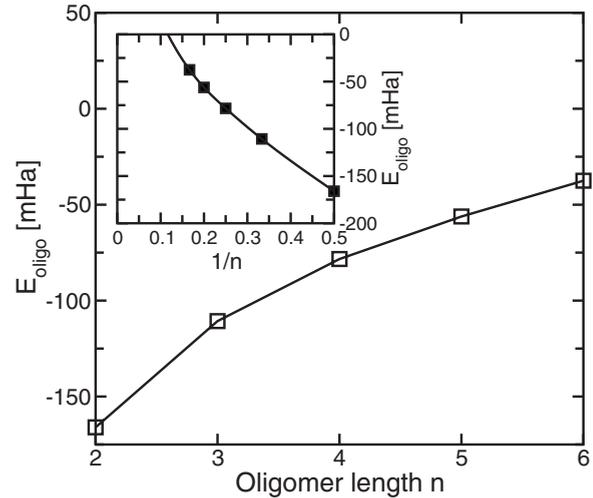

FIG. 4. Oligomerization energy of PDPA as a function of oligomer length. The inset presents the same data with respect to the inverse number of repeat units. The full line represents a cubic-spline fit to the calculated values, indicating that structures longer than eight repeat units will be unstable.

$C=C$ and $C—C$ bonds, respectively. This finally leads to the breaking of the single bond and the subsequent transformation of the double bond into a triple bond, converting the system into individual diphenyl acetylene molecules as indicated by the fact that the binding energy is approaching zero.

For comparison, we perform the same calculation for PA. Kahlert and co-workers[28] measured the lattice parameter as well as $C=C$ and $C—C$ bond lengths to be 2.455, 1.36, and 1.45 Å, respectively, while Yannono et al.[29] reported on the basis of NMR results double and single bond lengths of 1.36 and 1.44 Å, respectively. Our results, shown in Fig. 3, demonstrate, as expected, that the system is bound, with the theoretical lattice parameter being 2.475 Å, and the corresponding values of r_s=1.42 Å, r_d=1.38 Å. Both, theory and experiment exhibit nonzero bond alternation, which is fully consistent with Peierl's theorem,[30] stating that one-dimensional metals undergo a lattice distortion to minimize their energies, thus becoming band-gap materials. However, the magnitude of bond alternation, Δr=0.04 Å, found by our calculations is roughly a factor of two smaller than the experimental value.[28,29] This underestimation of bond alternation by DFT calculations is a well-known problem, discussed earlier by various authors.[31]

Realizing that the PDPA polymer is not stable, the question arises what limits the length of its oligomers. To this extent we study the energetics as a function of molecular size, considering two to six repeat units. For each of these structures, the geometry is optimized and the results are summarized in Table I. We note that all the oligomers are found to be invariant under inversion symmetry, exhibiting point group C_i.

Their oligomerization energies, E_{oligo}, as defined earlier, are displayed for these representatives in Fig. 4, exhibiting a decrease with increasing molecular size. To highlight the instability with larger oligomer length, we have plotted the energy as a function of inverse length, i.e., $1/n$ in the inset of the figure. Here, extrapolation clearly indicates that the for-

mation energy will become positive for $n > 8$. This is in excellent agreement with experimental findings,[12] where the longest oligomers have been estimated to consist of seven repeat units. Although It would be interesting to perform these calculations also for longer oligomers, at present it is computationally not feasible.

Analyzing the structural parameters, we observe a clear trend for the bond distances. Single as well as double bond lengths not only increase with the oligomer length, but also for a given oligomer they increase going from the outer PDPA repeat units toward the innermost ones. For example, in PDPA-6, r_d^1=1.39 Å and r_d^3=1.44 Å differ by as much as 0.05 Å while r_s increases from 1.52 to 1.56 Å at the same time. The latter value signalizes the bond breaking for larger oligomers as found for the polymer before. In contrast, for the PA oligomers the corresponding values all lie in the range of the polymer bond lengths exhibiting only small variations. The different bond lengths are reflected in the behavior of the bond alternation along the backbone. For example, Δr for the innermost bonds in PDPA-6 is 0.12 Å, while it is only half as large in PA-6. These results are in clear contrast to previous model calculations.[11]

The instability of longer oligomers is also reflected by the orientation of the phenyl rings with respect to the backbone, what is evident from Fig. 5 showing the relaxed geometry of PDPA-6. While at the innermost repeat units the phenyl groups take a nearly standing position with respect to the x axis, the outer ones are leaning toward the outside. This is demonstrated by the angle $\alpha(\beta)$, dramatically decreasing (increasing) from the left to the right.

Another interesting aspect concerns the torsion angle, δ, of the phenyl ring with respect to the polyene plane. In contrast to previous work assuming it close to 30°,[11] we predict much larger values, ranging from 56° to more than 90°. This appears counterintuitive at the first sight, because one would expect that such large torsion angles would destroy the conjugation between the backbone and the phenyl rings. This

TABLE I. Structural parameters for the oligomers of PDPA and PA, respectively. For definitions of the angles see Fig. 1. Bond lengths r_d and r_s as well as bond alternations Δr are given in Å. The superscripts denote the index of the repeat unit. For PDPA-2, the numbers in parentheses are results obtained with PBE0, while all other data are based on PBE.

	PDPA-2	PDPA-3	PDPA-4	PDPA-5	PDPA-6	PA-2	PA-3	PA-4	PA-5	PA-6
r_d^1	1.37 (1.37)	1.38	1.38	1.38	1.39	1.35	1.35	1.35	1.35	1.35
r_d^2	1.37 (1.37)	1.40	1.41	1.42	1.43	1.35	1.36	1.37	1.37	1.37
r_d^3		1.38	1.41	1.43	1.44		1.35	1.37	1.37	1.37
r_d^4			1.38	1.42	1.44			1.35	1.37	1.37
r_d^5				1.38	1.43				1.35	1.37
r_d^6					1.39					1.35
r_s^1	1.48 (1.49)	1.49	1.50	1.51	1.52	1.45	1.44	1.44	1.44	1.44
r_s^2		1.49	1.51	1.53	1.55		1.44	1.44	1.43	1.43
r_s^3			1.50	1.53	1.56			1.44	1.43	1.43
r_s^4				1.51	1.55				1.44	1.43
r_s^5					1.52					1.44
Δr^1	0.11 (0.12)	0.11	0.12	0.13	0.13	0.10	0.09	0.09	0.09	0.09
Δr^2		0.09	0.10	0.11	0.12		0.08	0.07	0.06	0.06
Δr^3			0.09	0.10	0.12			0.07	0.06	0.06
Δr^4				0.09	0.11				0.07	0.06
Δr^5					0.09					0.07
α^1	134.0° (133.7°)	138.8°	141.6°	143.3°	143.4°	121.2°	121.1°	121.2°	121.1°	121.3°
α^2	113.2° (113.2°)	120.8°	124.7°	126.7°	127.6°	119.5°	118.7°	118.8°	118.8°	118.7°
α^3		108.3°	115.4°	119.0°	120.1°		119.1°	118.5°	118.5°	118.4°
α^4			105.6°	112.6°	115.3°			119.0°	118.4°	118.4°
α^5				104.0°	111.0°				119.0°	118.3°
α^6					103.6°					119.0°
β^1	112.2° (112.2°)	109.2°	107.2°	105.9°	105.9°	117.1°	117.2°	117.1°	117.1°	117.1°
β^2	119.8° (119.7°)	112.7°	108.9°	106.5°	105.7°	116.4°	116.8°	117.0°	116.9°	117.1°
β^3		125.3°	117.2°	112.9°	110.8°		116.3°	117.0°	117.2°	117.3°
β^4			128.20°	120.1°	115.8°			116.4°	117.0°	117.1°
β^5				129.8°	121.6°				116.5°	117.2°
β^6					130.3°					116.4°
γ^1	113.8° (113.7°)	112.0°	111.2°	110.8°	110.7°	121.7°	121.7°	121.7°	121.7°	121.6°
γ^2	127.0° (127.0°)	126.5°	126.4°	126.8°	126.7°	124.1°	124.5°	124.2°	124.3°	124.2°
γ^3		126.4°	127.4°	128.1°	129.1°		124.6°	124.5°	124.3°	124.3°
γ^4			136.4°	127.3°	128.9°			124.6°	124.6°	124.5°
γ^5				126.2°	127.4°				124.5°	124.5°
γ^6					126.1°					124.6°
δ^1	56.3° (58.3°)	65.7°	72.4°	80.6°	78.0°					
δ^2	63.4° (63.7°)	77.1°	85.9°	92.1°	86.9°					
δ^3		68.1°	78.0°	84.1°	81.9°					
δ^4			71.3°	77.8°	79.2°					
δ^5				74.0°	75.8°					
δ^6					71.2°					

fact is, however, required by the small spacing between the rings provided by the polyene backbone. Only large torsion angles allow for an accommodation of the phenyl groups substituting the hydrogen atoms. A similar behavior is seen in rubrene, in which equally large torsion angles for the side phenyl rings have been reported.[32,33]

Before closing the discussion about the structural properties of PDPA's, we briefly comment on the choice of the exchange-correlation functional used in this work compared to hybrid functionals which have become popular these days. Such functionals, containing a certain percentage of Hartree-Fock (HF) exchange, give quite good results for conjugated
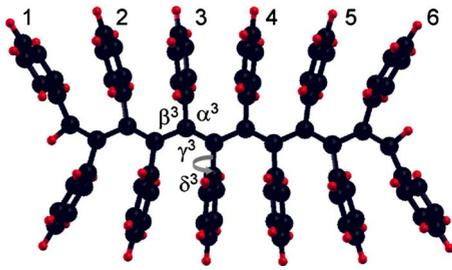
FIG. 5. (Color online) Relaxed geometry of PDPA-6. The angles are exemplary labeled for the third repeat unit. Note the inversion symmetry of the system.

polymers in several cases,[34] but there is no settled value for the amount of the HF exchange which describes all the properties equally well. To investigate whether one would obtain substantially different results using a hybrid functional, we have performed calculations for PDPA-2 using the PBE0[35] as implemented in the ESPRESSO program package[36] with 25% HF exchange. As the computing time for this molecule increases by two orders of magnitude compared to PBE, such calculations are not feasible for longer oligomers. As we see, however, from the comparison provided in Table I, the structural parameters as well as the oligomerization energy of PDPA-2 obtained with the two functional are in very good agreement with each other. The only notable differences are deviations of 3.5% in the value of δ^l and of about 9% in the oligomerization energy, E_{oligo} (166.05 mHa for PBE and 181.60 mHa for PBE0). These differences will not alter our conclusions in any significant manner. We believe that similar trends will also hold for longer oligomers, and, therefore, the choice of PBE in our case is well justified.

B. Optical absorption

Having discussed the structural properties, we now have a look at their impact on the electronic structure. To this extent, we compare the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of oligo-PDPA's and polyenes, presented in Table II. As expected, in both the systems, the energy gap decreases with the increase in molecular length. However, the gap is always found to be smaller in case of PDPA-n compared to PA-n, which is in agreement with experimental results[9,10] and earlier calculations.[11] Note that the presented values are Kohn-Sham gaps with the PBE exchange-correlation functional,[27] which are well known to be underestimated by roughly a factor of 2.

TABLE II. Kohn-Sham band gaps for various oligomers of PDPA and PA.

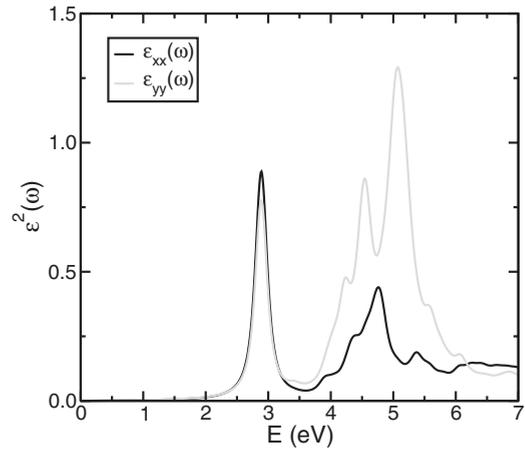| System	Kohn-Sham gap (eV)				
	n				
	2	3	4	5	6
PA	3.88	2.96	2.40	2.02	1.74
PDPA	2.88	2.38	2.00	1.80	1.52

FIG. 6. Dielectric tensor for PDPA-2 within the independent-particle approximation based on Kohn-Sham eigenstates.

Figure 6 shows the longitudinal and transverse components of the imaginary part of the dielectric tensor, $\epsilon^2_{xx}(\omega)$ and $\epsilon^2_{yy}(\omega)$, for PDPA-2. In both cases, the first peak occurs at 2.88 eV, which is precisely the Kohn-Sham gap, indicating that the lowest band-to-band transition is dipole-allowed. The spectra have been obtained within the independent-particle approximation, i.e., ignoring electron-hole interactions in the excitation process. In order to account for excitonic effects in the optical absorption, more sophisticated calculations based on the Bethe-Salpter equation would be needed, which are, however, outside the scope of the present work. Nevertheless, we expect that in parallel to the gaps, the exciton binding energies will also decrease with increasing oligomer length.[37–39]

Finally, we examine the presence of the significant transverse polarization in the HOMO-LUMO absorption[11,12] in
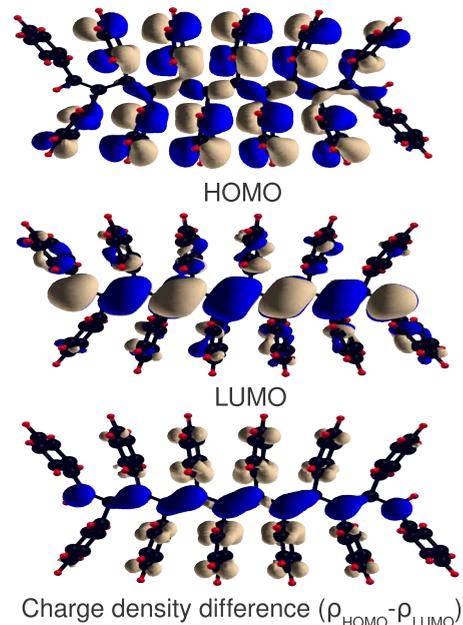

FIG. 7. (Color online) HOMO and LUMO wave functions (isovalue of ± 0.01), and corresponding charge density difference (isovalue of ± 0.001 e) plot. Dark (light) regions denote positive (negative) charge.

terms of charge densities. In light of the large torsion angles of the phenyl rings this observation needs to be better understood. For this purpose we present the wave functions of the HOMO and LUMO in Fig. 7. While the HOMO has significant charge density, both on the backbone as well as on the phenyl rings, the LUMO charge is much more confined to the backbone. This can be better understood when taking the difference between the two corresponding densities. Thus, HOMO→LUMO transitions in the optical spectra should involve significant charge transfer from the side groups to the backbone atoms, giving rise to transverse polarization. Moreover, the fact that the HOMO has substantial charge density on the phenyl rings also indicates that the large torsion angles do not destroy the electron conjugation between the backbone and the phenyl rings. A similar trend was also seen by Petrenko *et al.* for the case of rubrene.[32]

responding polymer cannot be formed. This finding is related to the large size of the phenyl rings which need to be accommodated within the length of a polyene dimer (repeat unit of the backbone) confirming and explaining experimental observations. The torsion angles of the phenyl rings range from 55° to 95°, ruling out an earlier conjecture about their values being 30° only. At the same time we have shown that such large torsion angles do not destroy the conjugation of electrons from the backbone with those of the phenyl rings. This fact is supported by the electron distribution of the HOMO which exhibits substantial charge density on the phenyl rings.

The energetics and the resulting structural properties of the oligo-PDPAs have been compared in detail with the corresponding situation in the parent-polymer, polyacetylene. It has been revealed that due to phenyl substitution, the bond alternation increases while the band gap decreases.

V. CONCLUSIONS

In summary, we have demonstrated by total-energy calculations based on density-functional theory that PDPA oligomers are only stable up to eight repeat units, while the cor-

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