Electronic structure and excitations in oligoacenes from *ab initio* calculations

Eugene S. Kadantsev^{a)} and M. J. Stott

Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada

Angel Rubio

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany;

Departamento de Física de Materiales, Facultad de Ciencias Químicas, UPV/EHU, Centro Mixto CSIC-UPV/EHU, E-20018 San Sebastián, Spain; and Donostia International Physics Center, E-20018 San

Sebastián, Spain

(Received 6 September 2006; accepted 21 February 2006; published online 3 April 2006)

Oligoacenes $C_{4n+2}H_{2n+4}$ ($n=2, \dots, 6$) are studied using a variety of *ab initio* methods. Density functional theory (DFT) optimized geometries were in good agreement with experiment. Vertical and adiabatic ionization potentials and electron affinities were computed with DFT and it was found that standard exchange-correlation (xc) functionals underestimate ionization potentials in oligoacenes. Possible reasons for this underestimation are discussed. Low lying electronic excitations were computed using time-dependent density functional theory, configuration interaction singles, and configuration interaction singles with approximate treatment of doubles. In agreement with earlier work, time-dependent DFT in conjunction with standard xc-energy functionals substantially underestimates the lowest (p) singlet-singlet electronic transition. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186999]

I. INTRODUCTION

Since its birth, the electronics industry has focused on reducing the size of electronic devices, in order to pack “as many transistors as possible” per unit area. At present, the size of electronic devices is approaching a fundamental limit and it is expected that individual molecules will soon play a vital role as active elements in the circuits. The development of electronic devices based on traditional materials such as silicon and germanium has for sometime been complemented with devices based on organic molecules. Organic electronics is attractive because it is cost effective and because the color of light emission/absorption can be easily adjusted.

Calculations based on *ab initio* methods can contribute to our understanding of photochemical and electrical properties of these organic materials and guide experimental research. Recently, a number of novel optoelectronic devices based on thin films of pentacene such as field-effect transistors^{1–3} (FETs) have been realized. Pentacene belongs to a class of polycyclic aromatic hydrocarbon (PAH) compounds known as oligoacenes which are planar sets of linearly arranged benzene rings with general formula $C_{4n+2}H_{2n+4}$. There is great interest in understanding the electronic structure of oligoacenes and, here, a comprehensive *ab initio* study of oligoacenes ($n=2, \dots, 6$) is reported (benzene is not considered in this study due to its special D_{6h} symmetry).

The number of electrons in the largest molecule of the series (hexacene) is 172. The method of choice for calculation of electronic structure and excitations in oligoacenes is Kohn-Sham (KS) density functional theory,^{4,5} (DFT) and, its

time-dependent extension, TDDFT (Refs. 6 and 7) due to the computational simplicity of these methods compared to methods based on approximations to the many-electron wave function. However, it is known that DFT within the local spin density approximation (LSDA) or generalized gradient approximation (GGA) strongly overestimates electrical response properties of molecular chains^{8,9} and the description of anions is sometimes problematic due to the incorrect asymptotic behavior of the exchange-correlation (xc) potential. There is hope to obtain better results with a hybrid approach in which a fraction of “exact” exchange is included in the xc-energy functional, but the standard hybrid xc-energy functional of quantum chemistry B3LYP (Ref. 10) did not include “extended” molecular chains such as oligoacenes in its molecular fit set. Clearly, applicability of standard DFT methods to investigation of long molecular chains, especially their optical properties, requires careful analysis and our work is a contribution in this area.

There have been several *ab initio* studies of the electronic structure of oligoacenes (and polyacenes).^{11–19} The most detailed study of their static properties was presented by Wiberg,¹² who examined structures and energies of oligoacenes $n=1, \dots, 5$ at B3LYP/6-311G(d,p) level. Wiberg found that carbon-carbon bond lengths are correlated with the charge density at the bond critical points and with the “ π -bond indices.” Wiberg also calculated vertical ionization potentials of oligoacenes $n=1, \dots, 4$ and concluded that “observed trends are reproduced.” Deleuze *et al.*¹⁴ determined vertical and adiabatic ionization potentials of oligoacenes $n=1, \dots, 6$ with an impressive accuracy of 0.02–0.07 eV using many-body perturbation theory (MBPT) and focal analysis. Excitation energies have also been calculated. Heinze

^{a)}Electronic mail: ekadants@mjs1.phy.queensu.ca

FIG. 1. Optimized geometries of oligoacenes (D_{2h} symmetry and 1A_g electronic state). (a) naphthalene; (b) anthracene; (c) naphthacene; (d) pentacene; and (e) hexacene. The bond lengths are in Å. Geometries are optimized with 6-311++G(d,p) basis set. EXP—x-ray experimental data. Naphthalene and anthracene: Crystallographic refinements of Brock *et al.* (Ref. 48). Tetracene: X-ray data obtained in Ref. 49 and reevaluated in Ref. 50. Pentacene: X-ray data obtained in Ref. 51 and reevaluated in Ref. 50.

*et al.*¹⁵ presented TDDFT singlet-singlet and singlet-triplet vertical excitation energies of oligoacenes computed with LSDA and compared theory and experiment up to $n=5$. Grimme and Parac¹⁶ computed the two lowest lying singlet-singlet excitation energies using TDDFT and the time-

dependent coupled cluster method with approximate treatment of double excitations²⁰ (CC2) and compared the results of their calculation to the experimental data up to $n=6$. They concluded that TDDFT in conjunction with standard xc-energy functionals such as GGAs and hybrid methods

FIG. 2. Carbon-carbon bond alternation patterns in naphthalene (upper panel) and pentacene (lower panel) as functions of y (the axis of growth). All bonds are in Å. $R=1.40$ Å is subtracted from each carbon-carbon bond length. The y coordinates of bonds that extend along the Oy axis such as C11–C12 and C1–C6 in naphthalene are obtained by projecting the bond midpoint. Left column—B3LYP calculation; right column—experimental results (Refs. 48–51). The bond alternation patterns computed with DFT methods strongly resemble the experimental patterns in the cases of naphthalene and anthracene which are not shown here and in pentacene.

strongly underestimates the energy of the transition between occupied and unoccupied valence π orbitals ($\pi \Rightarrow \pi^*$ transition). Transitions of this type were thought to be described fairly well within TDDFT framework.

In this work a detailed and systematic study of oligoacenes $n=2, \dots, 6$ is presented. Equilibrium geometries, ground state energies, ionization potentials (IEs), and electron affinities (EAs) are computed using a variety of xc-energy functionals. Evaluation of the accuracy of DFT methods for calculation of IE and EA is especially important since their difference is related to molecular hardness, an analog of the band gap for localized molecular systems. The effect of carbon-carbon bond alternation on the total energy and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap is also investigated for the largest molecule of the series, hexacene.

The low lying singlet-singlet and singlet-triplet electronic excitations were computed (see Appendix) using TD-DFT, an approach which is justified by the Runge-Gross theorem.⁶ The vertical excitation energies within linear combination of atomic orbital (LCAO) formalism are obtained from equations of Casida⁷ which have been coded in most quantum chemistry programs.^{21–23} In this work, results are reported for 16 lowest singlet-singlet and singlet-triplet excitation energies using standard GGA-type and hybrid xc-energy functionals.

Excitation energies are also presented using two approximate many-electron wave function approaches: configuration interaction singles²⁴ (CIS) and CIS with approximate treatment of doubles [CIS(D)].²⁵ In the CIS method, the excited state wave function is represented as a linear combination of all singly excited determinants with a determinant composed of Hartree-Fock orbitals as a reference. The CIS method is mostly of qualitative value as ≈ 1 eV overestimations in the excitation energies are common. However, when CIS is cor-

rected using second-order perturbation theory,²⁵ the errors in the excitation energies are substantially reduced.

II. RESULTS

A. Computational details

Calculations were performed with the GAUSSIAN 03 electronic structure code²⁶ using a valence triple zeta basis set^{27,28} augmented with d - and p -polarization functions²⁹ on carbon and hydrogen, respectively, and diffuse functions³⁰ on both carbon and hydrogen [6-311++G(d,p)], giving a total of 22 basis functions per carbon ($5s12p5d$) and 7 basis functions per hydrogen ($4s3p$). This basis set adds diffuse functions to that used by Wiberg¹² as these are anticipated to be important in calculation of excitation energies. Tests were performed with a smaller and a larger basis to assess the effects of basis set incompleteness. Tight convergence criteria were used to terminate the self-consistent-field (SCF) pro-

TABLE I. Effect of carbon-carbon bond alternation on the energy and the HOMO-LUMO gap of hexacene. B3LYP/6-311++G(d,p) calculation. $q=1$ —“fully alternated” (optimized) structure and $q=0$ —all carbon-carbon bond lengths are equal to 1.40 Å except those that are parallel to Oz axis. $\Delta E(q)=E(q)-E(q=1)$ —energy difference with the energy of the fully optimized structure as a reference. $E_{\text{gap}}=\epsilon_{\text{LUMO}}-\epsilon_{\text{HOMO}}$ —HOMO-LUMO gap. $\Delta E_{\text{gap}}=E_{\text{gap}}(q)-E_{\text{gap}}(q=1)$ —shrinkage of HOMO-LUMO gap.

Hexacene ($C_{26}H_{16}$)				
q	E (a.u.)	ΔE (eV)	E_{gap} (a.u.)	ΔE_{gap} (eV)
1.00	-1000.6643	0.00	0.0653	0.00
0.75	-1000.6637	0.02	0.0631	-0.06
0.50	-1000.6620	0.06	0.0608	-0.12
0.25	-1000.6593	0.14	0.0586	-0.18
0.00	-1000.6555	0.24	0.0563	-0.24

FIG. 3. Density of electron states of hexacene in the energy region near the HOMO-LUMO gap. $\epsilon_{\text{LUMO}} = -2.98$ eV and $\epsilon_{\text{HOMO}} = -4.74$ eV. B3LYP/6-311+G(*d,p*) calculation. $q=1$ —fully optimized structure and $q=0$ —“partially” optimized structure (all carbon-carbon bond lengths are equal to 1.40 Å except those that are parallel to *Oz* axis).

cedure in all the calculations. The presence of diffuse functions in our basis set led to convergence problems for hexacene which were cured by performing geometry optimization with a smaller basis set and using the output (geometry and the corresponding SCF solution) as the initial guess for optimization with a larger basis set.

The LSDA calculations used the Vosko-Wilk-Nusair parametrization of the correlation energy (SVWN5).³¹ The Perdew-Burke-Ernzerhof³² (PBE) functional for exchange and correlation was adopted as a representative of the GGA class of functionals, and the B3LYP functional¹⁰ in its GAUSSIAN 03 implementation was used as a hybrid functional representative.

B. Geometry

The geometry optimization of oligoacenes assumed an initial D_{2h} symmetry and the singlet ground state. Axes were chosen with the oligoacenes lying in the *yz* plane and the *Oy* axis along the axis of linear growth of the molecule. The optimized carbon-carbon bond lengths obtained with different DFT xc functionals are shown in Fig. 1.

The B3LYP/6-311+G(*d,p*) geometry optimization is in good agreement with the B3LYP/6-311G(*d,p*) optimization of Wiberg¹² and that of Deleuze *et al.*:¹⁴ B3LYP/cc-pVTZ (naphthalene and anthracene) and B3LYP/cc-pVDZ (naphthacene, pentacene, and hexacene). The largest discrepancy with the results of Wiberg is 0.003 Å for the C12–C13 bond of pentacene. The calculated bond lengths tend to be slightly longer than those reported in Refs. 12 and 14, probably due to the presence of diffuse functions in the basis set.

Figure 1 shows that carbon-carbon bond lengths computed with DFT satisfy $R_{\text{LSDA}} < R_{\text{B3LYP}} < R_{\text{PBE}}$. Usually, LSDA carbon-carbon bond lengths are shorter than experimental ones and PBE bonds are longer. For naphthalene and anthracene B3LYP gives the best agreement between theory and experiment, and the maximum errors in carbon-carbon bond lengths are 0.006 and 0.005 Å, respectively. The measured bond lengths for naphthacene and pentacene are less accurate than those for naphthalene and anthracene, and no

TABLE II. Vertical ionization potentials (IE_v), adiabatic ionization potential (IE_a), vertical electron affinities (EA_v), and adiabatic electron affinities (EA_a) of oligoacenes $n=2, \dots, 6$ computed at the B3LYP/6-311+G(*d,p*) level. IE_{exp} —experimental IE (Ref. 37) and EA_{exp} —experimental electron affinity: naphthalene (Ref. 52), anthracene (Ref. 53), and naphthacene and pentacene (Ref. 54). All energies are in eV.

<i>n</i>	IE_v	IE_a	IE_{exp}	EA_v	EA_a	EA_{exp}
2	7.97	7.88	8.15	−0.32	−0.20	−0.20
3	7.16	7.09	7.41	0.49	0.59	0.53
4	6.62	6.56	6.97	1.06	1.14	1.07
5	6.23	6.18	6.61	1.47	1.54	1.39
6	5.94	5.90	6.36	1.78	1.84	

experimental data on the geometry of hexacene have been found. B3LYP and LSDA give the best agreement between theory and experiment for larger oligoacenes. For pentacene, the results of LSDA calculations seem to be in slightly better agreement with experiment than B3LYP results. The longest carbon-carbon bond is the “central” bond aligned along the *Oz* axis (such as C1–C2 bond in naphthalene and anthracene and C12–C13 in naphthacene). The other bonds parallel to *Oz* are also long and do not alternate. The shortest bond is always in the end rings of the oligomer, for example, the C11–C12 bond in naphthalene, C17–C18 in anthracene, and C23–C24 in naphthacene. This is also a region of localization of the HOMO orbitals.

DFT calculations for naphthalene, anthracene, and pentacene reproduce carbon-carbon bond alternation patterns observed experimentally. Figure 2 shows the bond alternation pattern for naphthacene and pentacene computed with the B3LYP (the left column) and the experimental pattern (the right column). The reported experimental bond alternation pattern for naphthacene differs from the observed patterns for other oligoacenes, e.g., the reported C24–C25 bond length is 1.46 Å, making it one of the two longest bonds in the molecule. DFT calculations give C24–C25 shorter than C1–C6 and C1–C2, a pattern consistent with bond alternation in other molecules of the series. Apart from the C24–C25 bond in naphthacene, DFT reproduces the experimental bond lengths quite well, and different functionals give qualitatively the same bond alternation pattern in agreement with experiment.

The persistence of bond alternation to larger oligoacenes remains to be seen. As the size of the oligoacene increases, the difference between the adjacent inclined bond lengths

TABLE III. Vertical ionization potentials (IE_v) computed with different exchange only functionals and Hartree-Fock. SCF energies are computed at B3LYP/6-311+G(*d,p*) optimized geometries. HF—Hartree-Fock method, xB3LYP—exchange part of the B3LYP functional, and xLSDA—exchange only LSDA. All energies are in eV.

<i>n</i>	HF	xB3LYP	xLSDA
2	6.96	6.91	6.90
3	6.16	6.11	6.10
4	5.57	5.57	5.56
5	5.13	5.18	5.18
6	4.78	4.89	4.89

decreases in the inner part of the chain. For example, for naphthalene $R(\text{C11}-\text{C12})-R(\text{C17}-\text{C18})=0.018 \text{ \AA}$ and for hexacene $R(\text{C17}-\text{C18})-R(\text{C23}-\text{C24})=0.009 \text{ \AA}$, and as the size increases it might be expected that geometries optimized at D_{2h} symmetry will resemble polyacene with equal bond lengths. However, it is possible that for some n the isomers of C_{2h} or C_{2v} symmetry become energetically more favorable with the chain then resembling E - and Z -distorted polyacenes, respectively.¹¹ According to tight-binding calculations of Niehaus *et al.* the Z -distorted structure becomes more favorable at $n=20$.

The effect of carbon-carbon bond alternation on the energy and the HOMO-LUMO gap has been investigated for the largest molecule of the series, hexacene, at the B3LYP/6-311++G(d,p) level. This was done by calculating the effect on the Kohn-Sham energy eigenvalues and the total energy of gradually “turning on” the bond alternation through a parameter q from a system where there is none ($q=0$), to the fully alternated system ($q=1$). The position of the hydrogen atoms and the carbons that define bonds parallel to Oz axis, such as C18–C19 or C24–C25, was fixed at their optimized values. The remaining carbon-carbon bonds had values between an average bond length $R_{\text{CC}}^{\text{av}}=1.40 \text{ \AA}$ and the optimized length $R_{\text{CC}}^{\text{opt}}$ for the particular bond. Accordingly

$$R_{\text{CC}}^{\text{av}} + q(R_{\text{CC}}^{\text{opt}} - R_{\text{CC}}^{\text{av}}), \quad q \in [0, 1]. \quad (1)$$

The results for different q values are summarized in Table I. The total energy drops as the bond alternation increases and there is a net lowering of the energy due to the relaxation of carbon-carbon bonds of about 0.25 eV. This decrease in energy is, however, a small portion of the binding energy which is ≈ 8.3 a.u. at the B3LYP/6-311++G(d,p) level. It also agrees well with conclusions of Ref. 11 which reported that the energy differences between different isomers of polyacene are of order ≈ 1 kcal/mol per unit cell (for hexacene, $6 \times 1 \text{ kcal/mol} = 0.26 \text{ eV}$).

The bond alternation widens the HOMO-LUMO gap in the Kohn-Sham eigenvalues as illustrated in Fig. 3 which shows the electron density of states in hexacene near the HOMO-LUMO gap. The discrete energy levels in Fig. 3 are artificially broadened by a Gaussian. The increase in the HOMO-LUMO gap due to the bond alternation leads to a lowering of the occupied energy eigenvalues, especially the HOMO, and consequently a lowering of the total energy, and an increase in the stability of the molecule. However, as in the case of the energy, the increase in the HOMO-LUMO gap due to the bond alternation is small. These results complement the rather general arguments of Longuet-Higgins and Salem^{33,34} who investigated bond length alternation in long conjugated chain molecules. They showed that the alternation in polyacetylene is a result of a Peierls instability in which an energy gap is formed at the Fermi energy of a half-filled valence band due to the additional periodicity. In contrast, for polyacenes, they found that the valence band is already full and whether or not bond alternation occurs depends on the details of the electronic structure.

C. Ionization potentials and electron affinities

The IE and EA which may be obtained from ground state DFT are quantities affecting the optical properties. These have been computed as the energy differences between the appropriate charged species and neutral molecules using the geometry optimized at B3LYP/6-311++G(d,p) level as the reference. The results for IEs and EAs at the B3LYP/6-311++G(d,p) level are summarized in Table II. The table with the total energies, binding energies, zero-point energy corrections, and HOMO-LUMO KS eigenvalues computed with different xc-energy functionals at the respective optimized geometries can be obtained from the authors.

Results for the vertical IE for oligoacenes $n=2, \dots, 4$ are in good agreement with those reported by Wiberg,¹² with the largest discrepancy being 0.1 eV for $n=2$. The adiabatic IEs are 0.1 eV or less below the corresponding IE_v with the difference decreasing as the size of the chain increases due to the “delocalization” of the excess positive charge. The general trend of the B3LYP results agrees with experiment with the IE decreasing as the size of the chain increases, but both IE_α and IE_v underestimate the experimental values and the discrepancy grows with the size of the oligoacene, reaching 0.4 eV for hexacene. Calculations with a larger Gaussian basis set [6-311++G(3df,3pd)] gave results for $n=2$ and 3 that differed from those in Table II by 0.01 eV, verifying that the discrepancy in the ionization potential between B3LYP theory and experiment is not an artifact of the basis set incompleteness.

Possible causes of the underestimation of IEs have been investigated. It does not seem to be a consequence of the “hybrid” nature of B3LYP since GGA (PBE) calculation of IEs gave results that are ≈ 0.05 eV less than the corresponding B3LYP results. LSDA [SVWN5/6-311++G(d,p)] calculations of IEs have also been performed at the B3LYP optimized geometries. Since LSDA tends to overbind, it might be expected to overestimate IEs and, indeed, LSDA was found³⁵ to overestimate ionization potentials for the G2-1 data set. The results for the oligoacenes are 8.18, 7.37, 6.83, 6.44, and 6.15 eV for $n=2-6$, respectively, which, apart from naphthalene, are still underestimates, although the agreement with experiment is rather good, for the smaller molecules. Furthermore, residual exchange self-interaction does not significantly affect the IEs of the oligoacenes. Table III list results of Hartree-Fock calculations, in which exchange self-interaction is eliminated, and DFT calculations using the exchange only parts of B3LYP and LSDA, which include some residual self-interaction. Table III shows that the elimination of errors due to self-interaction would not remove the discrepancy in the IEs; in fact, the contrary, the self-interaction error tends to increase the IEs. It seems likely that a better treatment of electron correlation is needed to reproduce experimental IEs.

The electron affinities obtained using B3LYP are also listed in Table II along with observed values. The agreement with experiment is much better than for the IEs, for the smaller acenes where the vertical and adiabatic energies bracket the experimental value. It should be noted that the Kohn-Sham HOMO eigenvalue of the anions is positive up

FIG. 4. First two electronic excitations in oligoacenes: the p and α bands as a function of number of oligo-units. Note a larger “red shift” in the excitation energy for the p band as the size increases.

to and including naphthalene. However, the finite basis set technique employed in this study leads to the artificial stabilization of the SCF solution.³⁶

D. Excitation energies

Sixteen lowest singlet-singlet and singlet-triplet excitation energies of oligoacenes $n=2, \dots, 6$ computed with TDDFT using a GGA-type and the hybrid B3LYP xc-energy functional are listed in the Appendix. The excitation energies were computed for the geometry optimized at the B3LYP/6-311++G(d,p) level. CIS (Ref. 24) and CIS(D) (Ref. 25) methods were also used to calculate some excitations. Test showed that increasing the basis set from 6-311++G(d,p) to 6-311++G(3 df ,3 pd) changed the excitation energies by less than 0.04 eV, with the low lying excitation energies tending to decrease as the basis set was increased.

Three low lying absorption bands labeled p , α , and β are observed in oligoacenes.³⁷ The p band is polarized along the short axis of the oligomers and the α and β bands along the long axis. The intensity of the β band is the strongest followed by the p and α bands. The orders of the observed frequencies are α , p , and β for naphthalene, and p , α , and β in the other $n=3, \dots, 6$ oligoacenes. The p excitation corresponds to the HOMO-LUMO transition and the α and β transitions involve mainly HOMO-1 to LUMO and HOMO to LUMO+1 for naphthalene and anthracene, and HOMO-2 to LUMO and HOMO to LUMO+2 for naphthalene, pentacene, and hexacene. All three transitions are between occupied and unoccupied π -type molecular orbital ($\pi \Rightarrow \pi^*$) transitions. The results of calculations for these three bands are summarized in Table IV.

The theoretical results of Heinze *et al.*¹⁵ and Grimme and Parac¹⁶ are also listed in Table IV, along with the experimental results of Biermann and Schmidt³⁷ for oligoacenes in trichlorobenzene solution and include corrections for solvent

effects. The energies of the vibrational 0-0 components of UV transitions were estimated and extrapolated to the gas phase by adding 350 cm^{-1} (0.04 eV) to the α band and 1400 cm^{-1} (0.17 eV) to the p band.³⁷ Heinze *et al.*¹⁵ calculated excitation energies using LSDA whereas Grimme and Parac computed vertical excitation energies with the hybrid B3LYP functional. Grimme and Parac also reported excitation energies obtained using the coupled cluster method with approximate treatment of doubles²⁰ and performed geometry optimization in the excited states for oligoacenes $n=2, \dots, 4$ using TDDFT analytical forces.³⁸ The effects of geometrical relaxation in the excited states were then used to adjust experimental results³⁷ for vertical excitations. These adiabatic corrections became smaller as the size of the oligoacene increased, a trend similar for adiabatic corrections to IPs and EAs. We have not performed excited state geometry optimization, and the results in Table IV should be compared with the experimental excitation energies as adjusted by Grimme and Parac.

The B3LYP results are in very good agreement with those of Grimme and Parac,¹⁶ and PBE results are in close agreement with the LSDA results of Heinze *et al.*¹⁵ The results of the TDDFT calculations are in good agreement with experiment for the α and β bands, but there are systematic discrepancies for the p band. The results of our TDDFT and configuration interaction calculations for the p and α bands are illustrated in Fig. 4. The upper part of Fig. 4 also shows the HOMO-LUMO gap computed with the B3LYP xc functional.

The α excitation is described well with the B3LYP functional. The calculated energies are slightly above the experimental values as corrected by Grimme and Parac for $n>2$ and with a maximum discrepancy of 0.3 eV for naphthalene. The GGA (PBE) results for the α excitation are slight underestimates, but the overall agreement is equally good.

Similarly, GGA (PBE) and B3LYP describe the β band reasonably well, assuming that the adiabatic corrections are roughly the same as for the α band or smaller.

The TDDFT results for the p excitation are disappointing. As shown in Fig. 4 both the B3LYP and GGA energies lie significantly below the observed values and the disagreement with experiment increases with the size of the molecule, until for hexacene there is a 50% error. Görling³⁹ has shown that differences of Kohn-Sham eigenvalues are well-defined approximations for excitation energies and, indeed, Fig. 4 shows that the B3LYP HOMO-LUMO gap is very close to the p excitation energy in the case of oligoacenes, especially for small ones.

The CIS method strongly overestimates excitation energies for all the bands, especially the β band. The approximate treatment of doubles using the CIS(D) method improves the results, reducing the excitation energies except for the p excitation in naphthalene. The CIS(D) method is the only one of those used that gives the correct ordering of the p and α bands in naphthalene. It is also noteworthy that the CC2 (Ref. 20) results of Grimme and Parac seem to be superior to CIS(D) results for the p band and are almost identical for the α band.

TABLE IV. Excitation energies of $p(1^1B_{1u})$ short axis polarized, $\alpha(1^1B_{2u})$ —long axis polarized, and β bands (1^1B_{2u})—long axis polarized. Present work—calculations with 6-311++G(d,p) basis set at geometries optimized at B3LYP/6-311++G(d,p) level. Reference 15—LSDA calculation of Heinze *et al.* Reference 16 B3LYP calculation of Grimme and Parac. Expt.—excitation energies measured by Biermann and Schmidt (Ref. 37) and extrapolated to the gas phase as described in the text.

		Excitation energy (eV)								
Method transition		Reference 15 LSDA	Present work				Reference 16			Reference 37 Expt.
			GGA	B3LYP	CIS	CIS(D)	B3LYP	CC2	Expt. ^a	
Naphthalene (C ₁₀ H ₈)										
$p(1^1L_a)$	1^1B_{1u}	4.12	4.09	4.35	5.08	5.27	4.38	4.88	4.66	4.38
$\alpha(1^1L_b)$	1^1B_{2u}	4.21	4.23	4.44	5.22	4.49	4.47	4.46	4.13	4.03
$\beta(2^1L_b)$	2^1B_{2u}	5.69	5.68	5.85	6.89	6.24				5.62
Anthracene (C ₁₄ H ₁₀)										
$p(1^1L_a)$	1^1B_{1u}	2.96	2.94	3.21	4.11	4.05	3.21	3.69	3.60	3.38
$\alpha(1^1L_b)$	1^1B_{2u}	3.60	3.62	3.84	4.62	3.93	3.87	3.89	3.64	3.57
$\beta(2^1L_b)$	2^1B_{2u}	4.93	4.93	5.14	6.21	5.49				4.86
Naphthacene (C ₁₈ H ₁₂)										
$p(1^1L_a)$	1^1B_{1u}	2.19	2.18	2.44	3.37	3.22	2.43	2.90	2.88	2.71
$\alpha(1^1L_b)$	1^1B_{2u}	3.21	3.23	3.46	4.20	3.58	3.47	3.52	3.39	3.32
$\beta(2^1L_b)$	2^1B_{2u}	4.38	4.38	4.63	5.69	4.96				4.52
Pentacene (C ₂₂ H ₁₄)										
$p(1^1L_a)$	1^1B_{1u}	1.65	1.64	1.90	2.81	2.64	1.89	2.35	2.37	2.23
$\alpha(1^1L_b)$	1^1B_{2u}	2.95	2.95	3.20	3.91	3.34	3.21	3.27	3.12	3.05
$\beta(2^1L_b)$	2^1B_{2u}	3.96	3.96	4.24	5.27	4.57				4.14
Hexacene (C ₂₆ H ₁₆)										
$p(1^1L_a)$	1^1B_{1u}	1.25	1.24	1.50	2.39	2.23	1.49	1.95	2.02	1.90
$\alpha(1^1L_b)$	1^1B_{2u}	2.76	2.76	3.01	3.69	3.17	3.02	3.09	2.87	2.80
$\beta(2^1L_b)$	2^1B_{2u}	3.64	3.64	3.94	4.95	4.27				

^aExpt.—experimental energies from Ref. 37 as adjusted by Grimme and Parac to include effects of geometrical relaxation in the excited states (Ref. 16).

These results support the conclusion of Grimme and Parac¹⁶ in that it appears that TDDFT with common xc functionals describes reasonably well α and β electronic excitations in oligoacenes but strongly underestimates the p excitation energy. The origin of this difficulty with the p band is likely due to the deficiencies in both the xc potential and the xc kernel. It has been known for sometime that the position of the p band correlates linearly with the first ionization potential.⁴⁰ It was shown that the LSDA reproduces experimental IEs of oligoacenes with an accuracy of 0.2 eV; however, its errors for the p band are much greater.

We conclude this discussion with brief mention of the singlet-triplet electronic excitations reported in the Appendix. These excitations are spin forbidden and a careful analysis is needed to interpret the experimental results. Whereas the TDDFT PBE calculation gives singlet-singlet excitation energies that are almost identical to those obtained by Heinze *et al.*¹⁵ with LSDA, the corresponding singlet-triplet excitation energies reported here differ substantially from those of Ref. 15. For example, the differences for the lowest lying 1^3B_{1u} excitation are 0.23 and 0.18 eV for naphthalene and anthracene, respectively. This discrepancy may be due to the rather old parameterization of the correlation energy used in Ref. 15. A stability analysis of the SCF solution of the restricted Kohn-Sham equations for oligoacenes was performed according to Ref. 41. The analysis for hexacene

shows the singlet-triplet instability⁴² at the B3LYP/6-311++G(d,p) level. No instability was found with the PBE functional. Baldo *et al.*⁴³ predicted similar external instabilities based on an analysis of Hartree-Fock solutions in the framework of the Pariser-Parr-Pople model.^{44–46}

III. CONCLUSIONS

The DFT study of the structure and optical properties of oligoacenes C_{4n+2}H_{2n+4} ($n=2, \dots, 6$) finds optimized geometries in agreement with experiment for naphthalene, anthracene, pentacene, and, with reservations, for naphthacene. The calculations give bond alternation which decreases in amplitude with n in the inner portion of the chain. The bond alternation is not a Peierls instability but leads to widening of a preexisting HOMO-LUMO gap and a lowering of the energy, although the contribution is a small portion of the binding energy. Ionization potentials and electron affinities were also calculated. It was found that DFT methods underestimated the ionization potentials in oligoacenes and that this underestimation is not due to the exchange self-interaction.

The lowest 16 vertical excitation energies were calculated using TDDFT with various xc-energy functionals. Although the measured α and β transitions are described well,

the energy of the lowest singlet-singlet p transition is underestimated which suggests the need for further improvement in the xc-energy functionals.

The calculation of the optical properties of oligoacenes is a challenge for DFT methods and a greatly improved treatment of electron correlation effects may be necessary, for example, a GW-based approach such as that discussed in Ref. 47 and the references therein.

ACKNOWLEDGMENTS

One of the authors (E.K.) thanks Dr. H. Schmider for stimulating discussions. The authors gratefully acknowledge HPCVL for its computing resources. The work was supported by the NSERC of Canada. Another author (A.R.) acknowledges the Humboldt Foundation under the Bessel research award (2005) and the EC Sixth Framework Network of Excellence NANOQUANTA (NMP4-CT-2004-500198) and Spanish MCyT.

APPENDIX: EXCITATION ENERGIES OF OLIGOACENES

Tables V–XIV contain the first 16 lowest excitation energies of oligoacenes $C_{4n+2}H_{2n+4}$, $n=2, \dots, 6$ computed with TDDFT [Perdew-Burke-Ernzerhof (GGA) and B3LYP], CIS, and CIS(D). Tran. is the symmetry of the excited state, ω is the excitation energy in eV, and f is the oscillator strength. All singlet-triplet excitations are “spin forbidden” ($f=0$).

TABLE V. Singlet-singlet excitation energies of naphthalene ($C_{10}H_8$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Naphthalene ($C_{10}H_8$) method								
GGA			B3LYP			CIS		CIS (D)
Tran.	ω (eV)	f	Tran.	ω (eV)	f	Tran.	ω (eV)	ω (eV)
1 $^1B_{1u}$	4.09	0.04	1 $^1B_{1u}$	4.35	0.06	1 $^1B_{1u}$	5.08	5.27
1 $^1B_{2u}$	4.23	0.00	1 $^1B_{2u}$	4.44	0.00	1 $^1B_{2u}$	5.22	4.49
1 $^1B_{3g}$	5.01	0.00	1 1A_u	5.25	0.00	1 1A_u	5.75	5.60
1 1A_u	5.06	0.00	1 $^1B_{3g}$	5.50	0.00	1 $^1B_{1g}$	6.09	5.96
1 $^1B_{2g}$	5.36	0.00	1 $^1B_{2g}$	5.57	0.00	1 $^1B_{2g}$	6.17	6.00
1 $^1B_{1g}$	5.42	0.00	1 $^1B_{1g}$	5.60	0.00	1 $^1B_{3g}$	6.43	6.35
2 $^1B_{2u}$	5.68	1.14	2 $^1B_{2u}$	5.85	1.25	1 $^1B_{3u}$	6.52	6.35
1 $^1B_{3u}$	5.78	0.01	1 $^1B_{3u}$	6.00	0.01	2 1A_u	6.76	6.55
1 1A_g	5.80	0.00	2 $^1B_{1u}$	6.06	0.19	2 $^1B_{3u}$	6.80	6.53
2 $^1B_{1u}$	5.85	0.14	1 1A_g	6.11	0.00	2 $^1B_{2u}$	6.89	6.24
2 $^1B_{1g}$	5.95	0.00	2 $^1B_{3u}$	6.18	0.02	2 $^1B_{1g}$	6.96	6.67
2 $^1B_{3u}$	5.98	0.02	2 1A_u	6.18	0.00	2 $^1B_{2g}$	7.11	6.71
2 1A_u	5.98	0.00	2 $^1B_{3g}$	6.18	0.00	1 1A_g	7.15	6.26
2 $^1B_{3g}$	6.01	0.00	2 $^1B_{1g}$	6.30	0.00	3 1A_u	7.18	7.06
3 $^1B_{1g}$	6.07	0.00	2 $^1B_{2g}$	6.38	0.00	2 $^1B_{1u}$	7.18	6.38
2 $^1B_{2g}$	6.14	0.00	3 $^1B_{1g}$	6.66	0.00	3 $^1B_{1g}$	7.41	7.17

TABLE VI. Singlet-singlet excitation energies of anthracene ($C_{14}H_{10}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Anthracene ($C_{14}H_{10}$) method								
GGA			B3LYP			CIS		CIS (D)
Tran.	ω (eV)	f	Tran.	ω (eV)	f	Tran.	ω (eV)	ω (eV)
1 $^1B_{1u}$	2.94	0.04	1 $^1B_{1u}$	3.21	0.06	1 $^1B_{1u}$	4.11	4.05
1 $^1B_{2u}$	3.62	0.00	1 $^1B_{2u}$	3.84	0.00	1 $^1B_{2u}$	4.62	3.93
1 $^1B_{3g}$	3.91	0.00	1 $^1B_{3g}$	4.50	0.00	1 $^1B_{2g}$	5.14	5.04
2 $^1B_{3g}$	4.55	0.00	1 $^1B_{2g}$	4.76	0.00	1 $^1B_{3u}$	5.39	5.28
1 $^1B_{2g}$	4.58	0.00	2 $^1B_{3g}$	4.83	0.00	1 1A_u	5.51	5.37
2 $^1B_{1u}$	4.65	0.00	1 1A_u	4.96	0.00	1 $^1B_{3g}$	5.72	5.57
1 1A_u	4.74	0.00	1 $^1B_{3u}$	4.98	0.00	2 $^1B_{1u}$	5.86	5.68
1 $^1B_{3u}$	4.81	0.00	2 $^1B_{1u}$	5.05	0.00	1 $^1B_{1g}$	5.93	5.83
2 $^1B_{2u}$	4.93	1.75	2 $^1B_{2u}$	5.14	1.99	2 $^1B_{2g}$	5.95	5.78
1 1A_g	5.13	0.00	2 $^1B_{2g}$	5.44	0.00	2 $^1B_{2u}$	6.21	5.49
2 1A_g	5.15	0.00	1 $^1B_{1g}$	5.47	0.00	3 $^1B_{2g}$	6.44	6.33
2 $^1B_{2g}$	5.25	0.00	1 1A_g	5.49	0.00	2 $^1B_{3u}$	6.45	6.33
3 $^1B_{1u}$	5.26	0.00	3 $^1B_{1u}$	5.73	0.08	2 1A_u	6.50	6.34
1 $^1B_{1g}$	5.28	0.00	4 $^1B_{1u}$	5.83	0.01	2 $^1B_{1g}$	6.61	6.22
2 $^1B_{3u}$	5.30	0.00	2 1A_g	5.88	0.00	1 1A_g	6.71	5.75
3 1A_g	5.45	0.00	2 $^1B_{3u}$	5.97	0.01	2 $^1B_{3g}$	6.72	5.25

TABLE VII. Singlet-singlet excitation energies of naphthacene ($C_{18}H_{12}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Naphthacene ($C_{18}H_{12}$) method								
GGA			B3LYP			CIS		CIS(D)
Tran.	ω (eV)	f	Tran.	ω (eV)	f	Tran.	ω (eV)	ω (eV)
1 $^1B_{1u}$	2.18	0.03	1 $^1B_{1u}$	2.44	0.05	1 $^1B_{1u}$	3.67	3.22
1 $^1B_{3g}$	3.04	0.00	1 $^1B_{2u}$	3.46	0.00	1 $^1B_{2u}$	4.20	3.58
1 $^1B_{2u}$	3.23	0.00	1 $^1B_{3g}$	3.62	0.00	1 1A_u	4.70	4.65
2 $^1B_{3g}$	3.61	0.00	2 $^1B_{3g}$	3.90	0.00	1 $^1B_{3g}$	4.85	4.62
2 $^1B_{1u}$	4.02	0.00	1 1A_u	4.43	0.00	1 $^1B_{1g}$	4.90	4.83
1 1A_u	4.26	0.00	1 $^1B_{1g}$	4.58	0.00	1 $^1B_{2g}$	5.07	4.96
3 $^1B_{3g}$	4.35	0.00	1 $^1B_{2g}$	4.58	0.00	1 $^1B_{3u}$	5.41	5.33
1 $^1B_{2g}$	4.36	0.00	2 $^1B_{1u}$	4.58	0.00	2 1A_u	5.42	5.28
2 $^1B_{2u}$	4.38	2.23	2 $^1B_{2u}$	4.63	2.69	2 $^1B_{3g}$	5.45	5.23
1 1A_g	4.39	0.00	3 $^1B_{3g}$	4.71	0.00	2 $^1B_{2u}$	5.69	4.96
3 $^1B_{1u}$	4.40	0.01	1 1A_g	4.85	0.00	2 $^1B_{1u}$	5.75	5.54
1 $^1B_{1g}$	4.41	0.00	3 $^1B_{1u}$	4.92	0.00	3 $^1B_{3g}$	5.85	4.29
2 1A_g	4.57	0.00	2 1A_u	4.93	0.00	2 $^1B_{2g}$	5.86	5.73
3 1A_g	4.72	0.00	1 $^1B_{3u}$	4.99	0.00	2 $^1B_{1g}$	5.87	5.78
2 1A_u	4.75	0.00	2 1A_g	5.21	0.00	3 1A_u	6.01	5.91
1 $^1B_{3u}$	4.80	0.00	4 $^1B_{1u}$	5.29	0.01	1 1A_g	6.08	4.98

TABLE VIII. Singlet-singlet excitation energies of pentacene ($C_{22}H_{14}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Pentacene ($C_{22}H_{14}$) method								
GGA			B3LYP			CIS		CIS(D)
Tran.	ω (eV)	f	Tran.	ω (eV)	f	Tran.	ω (eV)	ω (eV)
1 $^1B_{1u}$	1.64	0.02	1 $^1B_{1u}$	1.90	0.04	1 $^1B_{1u}$	2.81	2.64
1 $^1B_{3g}$	2.38	0.00	1 $^1B_{3g}$	2.94	0.00	1 $^1B_{2u}$	3.91	3.34
2 $^1B_{3g}$	2.91	0.00	1 $^1B_{2u}$	3.20	0.00	1 $^1B_{3g}$	4.13	3.87
1 $^1B_{2u}$	2.95	0.00	2 $^1B_{3g}$	3.20	0.00	1 $^1B_{2g}$	4.37	4.38
2 $^1B_{1u}$	3.36	0.00	2 $^1B_{1u}$	3.96	0.00	1 $^1B_{3u}$	4.55	4.52
3 $^1B_{1u}$	3.70	0.02	1 $^1B_{2g}$	4.20	0.00	1 1A_u	4.75	4.69
1 1A_g	3.88	0.00	2 $^1B_{2u}$	4.24	3.35	1 $^1B_{1g}$	5.01	4.96
2 $^1B_{2u}$	3.96	2.63	3 $^1B_{1u}$	4.25	0.00	2 $^1B_{2g}$	5.06	4.95
4 $^1B_{1u}$	3.97	0.02	1 $^1B_{3u}$	4.30	0.00	2 $^1B_{3g}$	5.11	3.58
3 $^1B_{3g}$	3.98	0.00	1 1A_u	4.33	0.00	2 $^1B_{1u}$	5.13	4.96
1 $^1B_{2g}$	4.03	0.00	1 1A_g	4.35	0.00	3 $^1B_{1u}$	5.27	4.99
1 1A_u	4.11	0.00	4 $^1B_{1u}$	4.46	0.01	2 $^1B_{2u}$	5.27	4.57
2 1A_g	4.13	0.00	3 $^1B_{3g}$	4.50	0.00	2 1A_u	5.41	5.30
1 $^1B_{3u}$	4.14	0.00	5 $^1B_{1u}$	4.51	0.05	2 $^1B_{3u}$	5.44	5.38
5 $^1B_{1u}$	4.15	0.00	2 $^1B_{2g}$	4.58	0.00	3 $^1B_{3g}$	5.53	5.31
3 1A_g	4.19	0.00	1 $^1B_{1g}$	4.65	0.00	1 1A_g	5.53	4.47

TABLE IX. Singlet-singlet excitation energies of hexacene ($C_{26}H_{16}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Hexacene ($C_{26}H_{16}$) method								
GGA			B3LYP			CIS		CIS (D)
Tran.	ω (eV)	f	Tran.	ω (eV)	f	Tran.	ω (eV)	ω (eV)
1 $^1B_{1u}$	1.24	0.02	1 $^1B_{1u}$	1.50	0.03	1 $^1B_{1u}$	2.39	2.23
1 $^1B_{3g}$	1.88	0.00	1 $^1B_{3g}$	2.42	0.00	1 $^1B_{3g}$	3.56	3.30
2 $^1B_{3g}$	2.37	0.00	2 $^1B_{3g}$	2.65	0.00	1 $^1B_{2u}$	3.69	3.17
1 $^1B_{2u}$	2.76	0.01	1 $^1B_{2u}$	3.01	0.01	1 1A_u	4.13	4.18
2 $^1B_{1u}$	2.80	0.00	2 $^1B_{1u}$	3.39	0.00	1 $^1B_{1g}$	4.28	4.30
3 $^1B_{1u}$	3.10	0.03	3 $^1B_{1u}$	3.69	0.01	1 $^1B_{2g}$	4.49	4.48
4 $^1B_{1u}$	3.38	0.02	4 $^1B_{1u}$	3.82	0.06	2 $^1B_{3g}$	4.53	3.04
1 1A_g	3.50	0.00	2 $^1B_{2u}$	3.94	3.96	2 $^1B_{1u}$	4.65	4.34
3 $^1B_{3g}$	3.52	0.00	1 1A_g	3.97	0.00	1 $^1B_{3u}$	4.69	4.68
2 $^1B_{2u}$	3.64	2.95	1 1A_u	4.03	0.00	2 1A_u	4.79	4.72
2 1A_g	3.78	0.00	1 $^1B_{1g}$	4.10	0.00	3 $^1B_{3g}$	4.92	4.78
3 1A_g	3.80	0.00	3 $^1B_{3g}$	4.11	0.00	2 $^1B_{2u}$	4.95	4.27
4 $^1B_{3g}$	3.81	0.00	1 $^1B_{2g}$	4.15	0.00	2 $^1B_{2g}$	5.08	4.99
5 $^1B_{3g}$	3.85	0.00	4 $^1B_{3g}$	4.28	0.00	1 1A_g	5.09	4.09
1 1A_u	3.87	0.00	2 1A_u	4.34	0.00	2 $^1B_{1g}$	5.10	5.08
5 $^1B_{1u}$	3.90	0.00	2 1A_g	4.37	0.00	3 $^1B_{1u}$	5.27	4.98

TABLE X. Singlet-triplet excitation energies of naphthalene ($C_{10}H_8$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Naphthalene ($C_{10}H_8$) method							
GGA		B3LYP		CIS		CIS(D)	
Tran.	ω (eV)	Tran.	ω (eV)	Tran.	ω (eV)	ω (eV)	
1 $^3B_{1u}$	2.85	1 $^3B_{1u}$	2.75	1 $^3B_{1u}$	2.60	3.50	
1 $^3B_{2u}$	3.84	1 $^3B_{2u}$	3.95	1 $^3B_{3g}$	4.02	4.75	
2 $^3B_{2u}$	4.03	1 $^3B_{3g}$	4.20	1 $^3B_{2u}$	4.23	4.47	
1 $^3B_{3g}$	4.25	2 $^3B_{2u}$	4.21	2 $^3B_{1u}$	4.66	4.87	
2 $^3B_{1u}$	4.33	2 $^3B_{1u}$	4.39	2 $^3B_{2u}$	4.85	5.14	
2 $^3B_{3g}$	4.98	1 3A_u	5.23	1 3A_g	5.28	5.80	
1 3A_u	5.03	1 3A_g	5.31	1 3A_u	5.67	5.59	
1 3A_g	5.25	2 $^3B_{3g}$	5.50	1 $^3B_{1g}$	6.03	5.94	
1 $^3B_{2g}$	5.33	1 $^3B_{2g}$	5.55	1 $^3B_{2g}$	6.11	5.99	
1 $^3B_{1g}$	5.39	1 $^3B_{1g}$	5.58	1 $^3B_{3u}$	6.42	6.32	
2 3A_g	5.59	2 3A_g	5.89	2 3A_u	6.73	6.54	
3 3A_g	5.68	1 $^3B_{3u}$	5.98	2 $^3B_{3u}$	6.75	6.53	
1 $^3B_{3u}$	5.76	3 3A_g	6.08	2 3A_g	6.76	6.76	
2 $^3B_{1g}$	5.79	2 3A_u	6.16	2 $^3B_{3g}$	6.87	6.73	
2 $^3B_{3u}$	5.96	2 $^3B_{3u}$	6.17	2 $^3B_{1g}$	6.88	6.65	
2 3A_u	5.96	2 $^3B_{1g}$	6.28	3 3A_u	6.99	7.00	

TABLE XI. Singlet-triplet excitation energies of anthracene ($C_{14}H_{10}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Anthracene ($C_{14}H_{10}$) method							
GGA		B3LYP		CIS		CIS(D)	
Tran.	ω (eV)	Tran.	ω (eV)	Tran.	ω (eV)	ω (eV)	
1 $^3B_{1u}$	1.92	1 $^3B_{1u}$	1.83	1 $^3B_{1u}$	1.84	2.62	
1 $^3B_{3g}$	3.33	1 $^3B_{3g}$	3.30	1 $^3B_{3g}$	3.16	3.93	
1 $^3B_{2u}$	3.33	1 $^3B_{2u}$	3.48	1 $^3B_{2u}$	3.82	4.02	
2 $^3B_{2u}$	3.48	2 $^3B_{2u}$	3.67	2 $^3B_{1u}$	4.03	4.65	
2 $^3B_{3g}$	3.88	2 $^3B_{1u}$	4.09	2 $^3B_{2u}$	4.30	4.57	
2 $^3B_{1u}$	4.07	3 $^3B_{1u}$	4.37	1 3A_g	4.62	5.18	
3 $^3B_{1u}$	4.28	2 $^3B_{3g}$	4.46	3 $^3B_{1u}$	4.69	4.87	
1 3A_g	4.55	1 3A_g	4.63	1 $^3B_{2g}$	5.08	5.03	
1 $^3B_{2g}$	4.56	1 $^3B_{2g}$	4.74	1 $^3B_{3u}$	5.35	5.27	
4 $^3B_{1u}$	4.68	1 3A_u	4.95	1 3A_u	5.45	5.36	
1 3A_u	4.72	1 $^3B_{3u}$	4.96	3 $^3B_{2u}$	5.68	6.04	
1 $^3B_{3u}$	4.78	4 $^3B_{1u}$	5.14	1 $^3B_{1g}$	5.88	5.82	
2 3A_g	4.84	2 3A_g	5.28	2 $^3B_{2g}$	5.91	5.78	
3 3A_g	4.99	3 3A_g	5.35	4 $^3B_{1u}$	6.21	6.06	
5 $^3B_{1u}$	5.12	2 $^3B_{2g}$	5.42	3 $^3B_{2g}$	6.32	6.29	
2 $^3B_{3u}$	5.17	1 $^3B_{1g}$	5.46	2 3A_g	6.36	6.21	

TABLE XII. Singlet-triplet excitation energies of naphthacene ($C_{18}H_{12}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Naphthacene ($C_{18}H_{12}$) method					
GGA		B3LYP		CIS	
Tran.	ω (eV)	Tran.	ω (eV)	Tran.	ω (eV)
1 $^3B_{1u}$	1.28	1 $^3B_{1u}$	1.16	1 $^3B_{1u}$	1.24
1 $^3B_{3g}$	2.55	1 $^3B_{3g}$	2.53	1 $^3B_{3g}$	2.46
1 $^3B_{2u}$	3.00	1 $^3B_{2u}$	3.16	2 $^3B_{1u}$	3.41
2 $^3B_{3g}$	3.02	2 $^3B_{2u}$	3.32	1 $^3B_{2u}$	3.54
2 $^3B_{2u}$	3.12	2 $^3B_{1u}$	3.52	2 $^3B_{2u}$	3.91
2 $^3B_{1u}$	3.51	2 $^3B_{3g}$	3.59	2 $^3B_{3g}$	3.96
3 $^3B_{3g}$	3.90	3 $^3B_{3g}$	3.96	1 3A_g	4.15
1 3A_g	3.95	1 3A_g	4.09	1 3A_u	4.65
3 $^3B_{1u}$	3.98	3 $^3B_{1u}$	4.30	3 $^3B_{1u}$	4.73
4 $^3B_{1u}$	4.03	1 3A_u	4.42	1 $^3B_{1g}$	4.87
1 3A_u	4.24	4 $^3B_{1u}$	4.55	1 $^3B_{2g}$	5.02
2 3A_g	4.31	1 $^3B_{1g}$	4.56	3 $^3B_{2u}$	5.16
1 $^3B_{2g}$	4.35	1 $^3B_{2g}$	4.57	1 $^3B_{3u}$	5.37
5 $^3B_{1u}$	4.39	2 3A_g	4.69	2 3A_u	5.38
1 $^3B_{1g}$	4.39	3 3A_g	4.83	3 $^3B_{3g}$	5.71
3 3A_g	4.44	4 $^3B_{3g}$	4.87	2 3A_g	5.72

TABLE XIII. Singlet-triplet excitation energies of pentacene ($C_{22}H_{14}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Pentacene ($C_{22}H_{14}$) method					
GGA		B3LYP		CIS	
Tran.	ω (eV)	Tran.	ω (eV)	Tran.	ω (eV)
1 $^3B_{1u}$	0.83	1 $^3B_{1u}$	0.63	1 $^3B_{1u}$	0.77
1 $^3B_{3g}$	1.96	1 $^3B_{3g}$	1.92	1 $^3B_{3g}$	1.88
2 $^3B_{3g}$	2.37	2 $^3B_{1u}$	2.92	2 $^3B_{1u}$	2.84
1 $^3B_{2u}$	2.76	2 $^3b_{3g}$	2.92	1 $^3B_{2u}$	3.36
2 $^3B_{2u}$	2.88	1 $^3B_{2u}$	2.95	2 $^3B_{3g}$	3.52
2 $^3B_{1u}$	2.91	2 $^3B_{2u}$	3.09	2 $^3B_{2u}$	3.64
3 $^3B_{1u}$	3.31	3 $^3B_{3g}$	3.62	1 3A_g	3.82
4 $^3B_{1u}$	3.37	1 3A_g	3.70	3 $^3B_{1u}$	3.89
1 3A_g	3.52	3 $^3B_{1u}$	3.85	1 $^3B_{2g}$	4.33
3 $^3B_{3g}$	3.57	4 $^3B_{1u}$	3.88	1 $^3B_{3u}$	4.52
5 $^3B_{1u}$	3.75	5 $^3B_{1u}$	3.94	1 3A_u	4.70
2 3A_g	3.90	1 $^3B_{2g}$	4.19	3 $^3B_{2u}$	4.74
3 3A_g	3.95	2 3A_g	4.23	4 $^3B_{1u}$	4.76
4 $^3B_{3g}$	3.96	1 $^3B_{3u}$	4.28	1 $^3B_{1g}$	4.98
1 $^3B_{2g}$	4.02	1 3A_u	4.33	2 $^3B_{2g}$	5.02
4 3A_g	4.05	3 3A_g	4.41	3 $^3B_{3g}$	5.03

TABLE XIV. Singlet-triplet excitation energies of hexacene ($C_{26}H_{16}$) computed with 6-311++G(d,p) basis set. Geometry is optimized at B3LYP/6-311++G(d,p) level.

Hexacene ($C_{26}H_{16}$) method					
GGA		B3LYP		CIS	
Tran.	ω (eV)	Tran.	ω (eV)	Tran.	ω (eV)
1 $^3B_{1u}$	0.49	1 $^3B_{1u}$	0.66 ^a	1 $^3B_{1u}$	0.41
1 $^3B_{3g}$	1.50	1 $^3B_{3g}$	1.43	1 $^3B_{3g}$	1.41
2 $^3B_{3g}$	1.87	2 $^3B_{1u}$	2.39	2 $^3B_{1u}$	2.33
2 $^3B_{1u}$	2.40	2 $^3B_{3g}$	2.41	2 $^3B_{3g}$	3.08
1 $^3B_{2u}$	2.59	1 $^3B_{2u}$	2.79	1 $^3B_{2u}$	3.23
3 $^3B_{1u}$	2.71	2 $^3B_{2u}$	2.93	2 $^3B_{2u}$	3.44
2 $^3B_{2u}$	2.71	3 $^3B_{3g}$	3.15	3 $^3B_{1u}$	3.58
4 $^3B_{1u}$	2.84	3 $^3B_{1u}$	3.31	1 3A_g	3.59
3 $^3B_{3g}$	3.11	4 $^3B_{1u}$	3.41	3 $^3B_{3g}$	3.82
1 3A_g	3.21	1 3A_g	3.42	1 3A_u	4.09
4 $^3B_{3g}$	3.51	5 $^3B_{1u}$	3.65	1 $^3B_{1g}$	4.26
2 3A_g	3.56	4 $^3B_{3g}$	3.75	3 $^3B_{2u}$	4.41
5 $^3B_{1u}$	3.56	2 3A_g	3.88	1 $^3B_{2g}$	4.45
5 $^3B_{3g}$	3.58	1 3A_u	4.02	4 $^3B_{3g}$	4.45
3 3A_g	3.62	1 $^3B_{1g}$	4.08	1 $^3B_{3u}$	4.67
6 $^3B_{3g}$	3.64	5 $^3B_{3g}$	4.09	2 3A_u	4.75

^a—computed with DFT as singlet-triplet energy difference.

- ¹H. E. Katz, J. Mater. Chem. **7**, 369 (1997).
- ²G. Horowitz, Adv. Mater. (Weinheim, Ger.) **10**, 365 (1998).
- ³S. F. Nelson, Y. Y. Lin, D. J. Gundlach, and T. N. Jackson, Appl. Phys. Lett. **72**, 1854 (1998).
- ⁴P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ⁵W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ⁶E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- ⁷M. E. Casida, in *Recent Advances in Density Functional Theory*, edited by D. P. Chong (World Scientific, Singapore, 1995), Vol. 1.
- ⁸S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).
- ⁹O. V. Gritsenko, S. J. A. van Gisbergen, P. R. T. Schipper, and E. J. Baerends, Phys. Rev. A **62**, 012507 (2000).
- ¹⁰A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- ¹¹J. Cioslowski, J. Chem. Phys. **98**, 473 (1993).
- ¹²K. B. Wiberg, J. Org. Chem. **62**, 5720 (1997).
- ¹³K. N. Houk, P. S. Lee, and M. Nendel, J. Org. Chem. **66**, 5517 (2001).
- ¹⁴M. S. Deleuze, L. Claes, E. S. Kryachko, and J.-P. François, J. Chem. Phys. **119**, 3106 (2003).
- ¹⁵H. H. Heinze, A. Görling, and N. Rösch, J. Chem. Phys. **113**, 2088 (2000).
- ¹⁶S. Grimme and M. Parac, Tech. Rep. Ser. - I. A. E. A. **4**, 292 (2003).
- ¹⁷J. E. Northrup, M. L. Tiago, and S. G. Louie, Phys. Rev. B **66**, 121404(R) (2002).
- ¹⁸T. A. Niehaus, M. Rohlfing, F. Della Sala, A. Di Carlo, and T. Frauenheim, Phys. Rev. A **71**, 022508 (2005).
- ¹⁹K. Hummer and C. Ambrosch-Draxl, Phys. Rev. B **71**, 081202(R) (2005).
- ²⁰O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
- ²¹C. Jamorski, M. E. Casida, and D. R. Salahub, J. Chem. Phys. **104**, 5134 (1995).
- ²²R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

- ²³R. E. Stratmann and G. E. Scuseria, J. Chem. Phys. **109**, 8218 (1998).
- ²⁴J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).
- ²⁵M. Head-Gordon, D. Maurice, and M. Oumi, Chem. Phys. Lett. **246**, 114 (1995).
- ²⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- ²⁷A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
- ²⁸R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
- ²⁹M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).
- ³⁰T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. V. R. Schleyer, J. Comput. Chem. **4**, 294 (1983).
- ³¹S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- ³²J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ³³H. C. Longuet-Higgins and L. Salem, Proc. R. Soc. London, Ser. A **251**, 172 (1959).
- ³⁴L. Salem and H. C. Longuet-Higgins, Proc. R. Soc. London, Ser. A **255**, 435 (1960).
- ³⁵M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
- ³⁶N. Rösch and S. B. Trickey, J. Chem. Phys. **106**, 8940 (1997).
- ³⁷D. Biermann and W. Schmidt, J. Am. Chem. Soc. **102**, 3163 (1980).
- ³⁸F. Furche and R. Ahlrichs, J. Chem. Phys. **117**, 7433 (2002).
- ³⁹A. Görling, Phys. Rev. A **54**, 3912 (1996).
- ⁴⁰W. Schmidt, J. Chem. Phys. **66**, 828 (1977).
- ⁴¹R. Bauernschmitt and R. Ahlrichs, J. Chem. Phys. **104**, 9047 (1996).
- ⁴²P.-O. Löwdin, Rev. Mod. Phys. **35**, 496 (1963).
- ⁴³M. Baldo, G. Piccitto, R. Pucci, and P. Tomasello, Phys. Lett. **95A**, 201 (1983).
- ⁴⁴R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).
- ⁴⁵R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 767 (1953).
- ⁴⁶J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).
- ⁴⁷G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
- ⁴⁸C. P. Brock, J. D. Dunitz, and F. L. Hirshfeld, Acta Crystallogr., Sect. B: Struct. Sci. **47**, 789 (1991).
- ⁴⁹J. M. Robertson, V. C. Sinclair, and J. Trotter, Acta Crystallogr. **14**, 697 (1961).
- ⁵⁰R. B. Campbell and J. M. Robertson, Acta Crystallogr. **15**, 289 (1962).
- ⁵¹R. B. Campbell, J. M. Robertson, and J. Trotter, Acta Crystallogr. **14**, 705 (1961).
- ⁵²S. A. Lyapustina, S. K. Xu, J. M. Nilles, and K. Bowen, J. Chem. Phys. **112**, 6643 (2000).
- ⁵³J. Schiedt and R. Weinkauf, Chem. Phys. Lett. **266**, 201 (1997).
- ⁵⁴L. Crocker, T. B. Wang, and P. Kebarle, J. Am. Chem. Soc. **115**, 7818 (1993).