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Geometry relaxation in singlet excited states of oligomers containing cyclopentadiene and fulvene and their cyano derivatives

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Abstract

Using the singles configuration interaction (CIS) theoretical approach, we investigated the nature of the geometric conformations and electronic transitions in π-conjugated oligo(cyclopentadiene)s and oligo(fulvene)s, and their cyano derivatives. Geometry optimizations were first carried out with the restricted Hartree–Fock (RHF/3-21G*) method which was followed by calculations of excitation energies using CIS (CIS/3-21G*) method. The trends in excitation energies as a function of chain lengths show that the band gaps in the cyano substituted compounds are lowered by approximately 0.5 eV relative to their parent polymers. The results of CIS/3-21G* oligomer calculations also show that delocalized singlet excited states are accompanied by a geometry relaxation in comparison to their ground state (HF) geometries.

Keywords: Cyclopentadiene; Configuration interaction; Fulvene

1. Introduction

Polymers and oligomers consisting of cyclopentadiene and fulvene (see Fig. 1) units are examples of conjugated systems. They are of interest because of their promise to yield conducting materials in either pure or doped form. The electronic and optical properties of conjugated organic polymers and oligomers have been reviewed extensively in a number of monographs and articles (see e.g. [1,2] and references within). In general, the presence of a small intrinsic band gap in conjugated materials could enhance their conductivity. For example, one such a polymer, poly(dicyanomethylene cyclopentadithiophene) (PCNTH) have been shown experimentally [3,4] to have a very small band gap (~0.8 eV). In our previous study [5], involving configuration interaction (singles) (CIS) approach [6], we investigated the excited state structures of oligo(acetylene) (OA), oligo(thiophene) OTH and oligo(dicyanomethylene cyclopentadithiophene) (OCNTH) to ascertain the changes that these systems undergo both as a result of increasing lengths and differences in chemical compositions. It was found that a band gap in the cyano-substituted OCNTH was lowered relative to the one found in OTH and that geometry relaxation phenomena played an important role in excited state of OA, OTH and OCNTH. The lowest singlet (experimental) excitation energies of OTH were well reproduced by the CIS method. In this work, this comparison serve as a calibration of the CIS approach for similar systems.

Since the presence of a cyano group in PCNTH has led to such significant lowering of an intrinsic band gap relative to the one found in PTH, other parent polymers have been considered as possible candidates for the cyano group bridging. In particular, there were early indications [7,8] that poly(dicyanomethylene cyclopentadicyclopentadiene) (PCNCY) and possibly poly(dicyanomethylene cyclopentadifulvene) (PCNFv) might have band gaps comparable to the one found in PCNTH. The parent polymers in this case are poly(cyclopentadiene) (PCY) and poly(fulvene) (PFv), respectively. In this work, we analyze the excited state structures of the oligo(cyclopentadiene) (OCY), oligo (dicyanomethylene cyclopentadicyclopentadiene) (OCNCY), oligo(fulvene) (OFv) and oligo(dicyanomethylene cyclopentadifulvene) (OCNFv) using the CIS approach. The monomers of oligo(*s-trans* acetylene) (*s-trans* OA), OCY, OCNCY, OFv and OCNFv are shown in Fig. 1.

In majority of theoretical studies that investigated the

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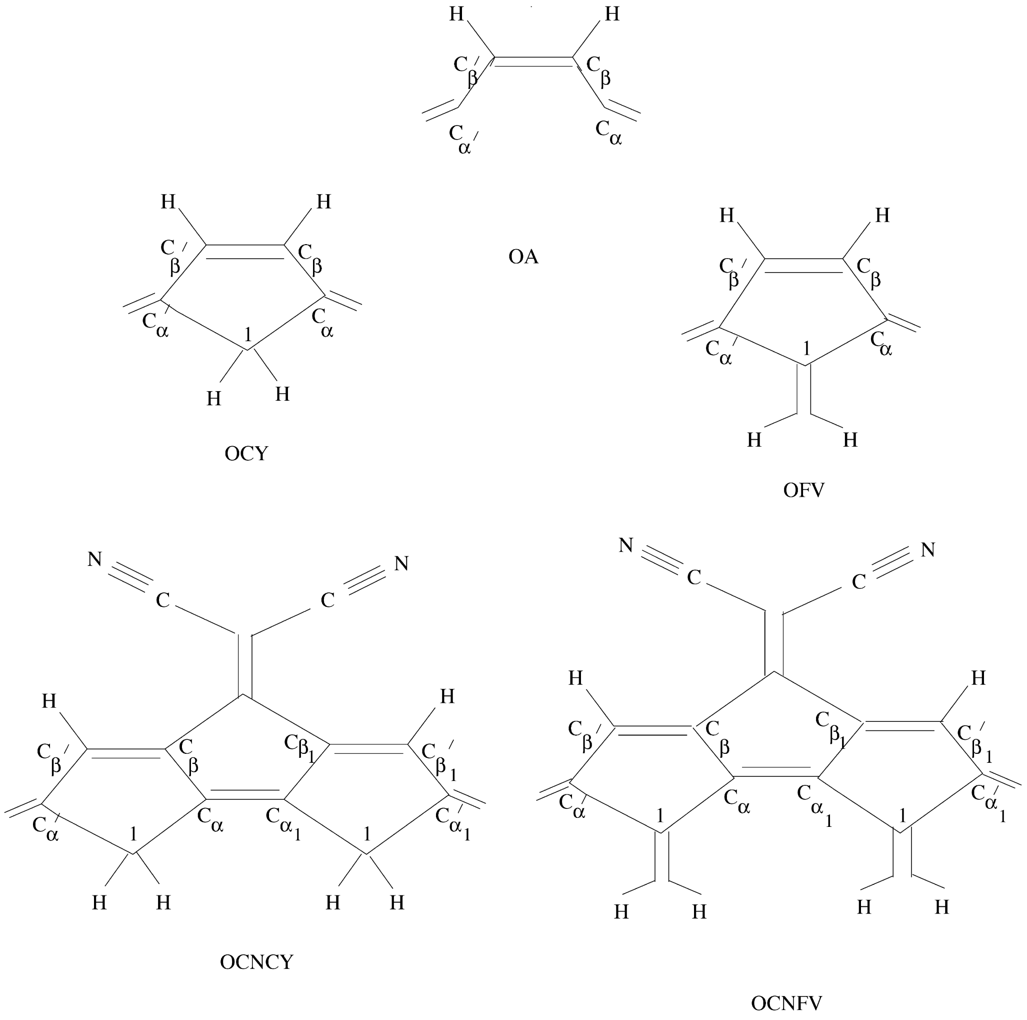


OA

OCY

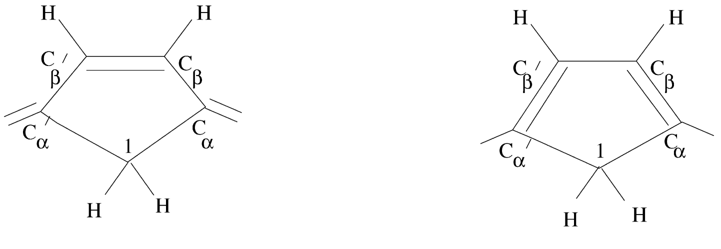
OFV

OCNCY

OCNFV

Fig. 1. Monomers of the π conjugated systems studied.

structure of cyclopentadiene [8–13] and fulvene [14–19] and their derivatives [8], the ground state geometry had an aromatic form similar to OTH and OCNTH (see Fig. 2, where the definitions for the structural forms, quinonoid and aromatic, are illustrated for OCY as an example). In few cases [7,20–22], where the stability of aromatic form relative to quinonoid form was examined, it was found that the quinonoid form of OCY, OCNCY, OFv and OCNFv was more stable. Interestingly, it was also found [7] that lower band gaps were obtained for the less stable mesomeric forms, i.e. for PT and PCNTH in their *s-trans* (quinonoid) forms and for PFv, PCY, PCNFv and PCNCY in *s-cis* (aromatic) structures. The band gaps for quinonoid PCY and PFv were theoretically estimated to be approximately 2 eV [20,22] and for PCNCY of the order of 2.5 eV [21]. This should be contrasted with the much smaller values predicted for band gaps for their aromatic forms (e.g. less than 1 eV for PCNCY [8]). Because of their greater stability we consider quinonoid forms of OCY, OCNCY, OFv and OCNFv (see Fig. 1) in this work. Earlier investigations employed semiempirical and empirical (Hückel) band structure theories to obtain band gaps. In the present



quinonoid OCY

aromatic OCY

Fig. 2. Monomers of quinonoid and aromatic forms of OCY.

Table 1
Comparison of singlet excitation energies (in eV) for different oligomers in their most stable (*anti* and *planar*) configuration

Method/basis set	Oligomer	OCY	OFv	OCNCY	OCNFv
RHF/3-21G*	Dimer	10.53	9.25	7.06	6.57
LSDA/3-21G*	Dimer	2.78	2.08	0.75	0.65
RCIS/3-21G* 1SCF	Monomer			4.24	4.11
RCIS/3-21G* (Opt)	Monomer	6.35	6.46	3.58	3.47
RCIS/3-21G* 1SCF	Dimer	5.81	4.80	3.32	3.03
RCIS/3-21G* (Opt)	Dimer	4.79	4.00	2.59	2.35
RCIS/6-31G* (Opt)	Dimer	4.61	3.85	2.44	2.20
RCIS/3-21G* (Opt)	Tetramer	3.36	3.05	2.57	2.34
RCIS/3-21G* (Opt)	Hexamer			2.54	2.32
RCIS/3-21G* (Opt)	Octamer	2.81	2.65		
RCIS/3-21G* (Opt)	Decamer	2.77			
RCIS/3-21G* (Opt)	12 Monomers	2.77			

work, ab initio CIS calculations have been consistently performed for all cyclopentadiene and fulvene based oligomers.

2. Methodology

Oligomers of length from one to eight monomers of *s-trans* OA, OCY and OFv, and from one to six monomers of OCNCY and OCNFv were optimized in planar geometry employing the ab initio molecular orbital theory at restricted Hartree–Fock (RHF) level for the ground state geometries and the closed-shell restricted CIS for the excited state structures. All calculations were performed using GAUSSIAN 94 [23]. Also, throughout this study (with one exception see below), the 3-21G* basis set has been used. The configuration interaction (CI) approach allows the inclusion of some correlation effects and its main advantage over other method such as density functional theory (DFT) is that it permits one to study the lattice relaxation phenomena in a more direct way.

The validity of using the RHF/3-21G* and CIS/3-21G* approaches (for the ground and excited state, respectively) was investigated in our previous work on similar systems [5] and a good agreement between experimental and CIS values was found both for the structural parameters and excitation energies.

Bond length alternation (denoted by δ_r) is an important parameter whose value has been closely linked to the size of the band gap [24]. It is defined as the average of the difference between the neighboring longer (single) and shorter (double) carbon–carbon bonds. The sign of δ_r indicates whether the system is in a quinonoid (positive) or an aromatic (negative) form. For OA, OCY and OFv unit cell δ_r is defined as [20]

$$\delta_r = \tfrac{1}{2}[(C_{\alpha'-\beta'}) - (C_{\beta'-\beta}) + (C_{\beta-\alpha}) - (C_{\alpha-\alpha'})],$$

and for the cyano-substituted derivatives (OCNCY and OCNFv) δ_r is given by

$$\delta_r = \tfrac{1}{4}[(C_{\alpha'-\beta'}) - (C_{\beta'-\beta}) + (C_{\beta-\alpha}) - (\text{Intracell}) + (C_{\alpha_1-\beta_1}) - (C_{\beta_1-\beta_1'}) + (C_{\beta_1'-\alpha_1'}) - (\text{Intercell})].$$

3. Results and discussion

The ground state HF and the lowest singlet excited state CIS fully optimized energies and geometries of the OCY,

Table 2
Bond lengths (in Å) and excitation energies for cyclopentadiene oligomers (OCY)

Oligomer/method	α'-β'	β'-β	β-α	Intra-cell	Inter-cell	δ_r	E_{cal} (eV)
Monomer (HF)	1.519	1.316	1.519				14.77
Monomer (CIS)	1.482	1.541	1.482				6.35
Dimer (HF)	1.520	1.323	1.472	1.323		0.173	10.53
Dimer (CIS)	1.512	1.373	1.406	1.415		0.065	4.79
Tetramer (HF)	1.520	1.324	1.471	1.325		0.171	8.52
	1.468	1.333	1.469		1.326	0.139	
Tetramer (CIS)	1.518	1.335	1.447	1.355		0.138	3.36
Octamer (HF)	1.520	1.324	1.471	1.325		0.171	7.72
	1.467	1.333	1.468		1.326	0.138	
	1.467	1.334	1.467	1.326		0.137	
	1.467	1.334	1.467		1.326	0.137	
Octamer (CIS)	1.519	1.325	1.467	1.329		0.166	2.81
	1.449	1.343	1.459		1.342	0.112	
	1.439	1.360	1.427	1.360		0.073	
	1.412	1.377	1.418		1.369	0.042	

From dimers on, because of the inversion symmetry, only bond lengths for half of the molecule are shown in each case.

Table 3
Bond lengths (in Å) and excitation energies for fulvene oligomers (OFv)

Oligomer/method	α'-β'	β'-β	β-α	Intra-cell	Inter-cell	δ_r	E_{cal} (eV)
Monomer (HF)	1.520	1.318	1.520				14.06
Monomer (CIS)	1.520	1.323	1.520				6.46
Dimer (HF)	1.507	1.322	1.483	1.342		0.163	9.38
Dimer (CIS)	1.502	1.343	1.446	1.443		0.081	4.00
Tetramer (HF)	1.504	1.322	1.485	1.346		0.161	7.92
	1.469	1.326	1.464		1.349	0.129	
Tetramer (CIS)	1.502	1.330	1.468	1.379		0.131	3.05
	1.417	1.372	1.409		1.414	0.020	
Octamer (HF)	1.503	1.322	1.485	1.346		0.160	
	1.464	1.326	1.469		1.349	0.129	7.37
	1.465	1.326	1.466	1.350		0.128	
	1.466	1.326	1.466		1.350	0.128	
Octamer (CIS)	1.503	1.323	1.483	1.350		0.157	
	1.456	1.334	1.455		1.365	0.106	2.65
	1.440	1.348	1.432	1.385		0.070	
	1.420	1.364	1.415		1.397	0.037	

From dimers on, because of the inversion symmetry, only bond lengths for half of the molecule are shown in each case.

OFv, OCNCY and OCNFv starting from their monomeric units (Fig. 1) are given in Tables 1–5. The systems considered are planar and in *anti* conformation (i.e. monomers point in opposite directions). For polymers (infinite linear chains), the translational symmetry requires that the unit (repeat) cell consist of two monomers. Hence in Tables 2–5 intra- and inter-cell distances are listed separately. The geometric parameters are labeled according to Fig. 1. The variation of the average bond length alternation, δ_r, along the backbone is also given in Tables 2–5.

3.1. Excitation energies

The excitation energies are one of the many features of a molecular excited state which are of interest to both physicists and chemists. For the conjugated systems the lowest (singlet) excited state often corresponds to a transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level and their excitation energies are red shifted with increasing chain length.

Table 4
Bond lengths (in Å) and excitation energies for dicyanomethylene cyclopentadiene oligomers (OCNCY)

Oligomer/method	α'-β'	β'-β	β-α	Intra-cell	Inter-cell	α_1-β_1	β_1-β'_1	β'_1-α'_1	δ_r	E_{cal} (eV)
Monomer (HF)	1.529	1.325	1.484	1.324		1.484	1.325	1.529		8.68
Monomer (CIS)	1.573	1.358	1.444	1.373		1.444	1.358	1.516		3.58
Dimer (HF)	1.529	1.324	1.483	1.325	1.329	1.479	1.335	1.471	0.162	
	1.471	1.335	1.480	1.325	1.329	1.483	1.324	1.529	0.162	7.06
Dimer (CIS)	1.527	1.327	1.474	1.341	1.380	1.454	1.384	1.407	0.108	2.59
	1.407	1.384	1.454	1.341	1.380	1.474	1.327	1.527	0.108	
Tetramer (HF)	1.471	1.335	1.480	1.326	1.329	1.479	1.335	1.472	0.144	6.54
Tetramer (CIS)	1.528	1.324	1.483	1.325	1.329	1.479	1.335	1.472	0.162	2.57
	1.471	1.335	1.479	1.326	1.331	1.478	1.336	1.470	0.143	
	1.468	1.338	1.469	1.342	1.381	1.454	1.385	1.406	0.088	
	1.406	1.385	1.453	1.342	1.381	1.473	1.328	1.526	0.106	
Hexamer (HF)	1.471	1.335	1.480	1.326	1.329	1.479	1.335	1.472	0.144	6.43
Hexamer (CIS)	1.528	1.324	1.483	1.325	1.329	1.478	1.335	1.472	0.162	2.54
	1.471	1.335	1.479	1.326	1.331	1.478	1.336	1.469	0.143	
	1.467	1.339	1.467	1.344	1.382	1.452	1.385	1.405	0.085	
	1.405	1.385	1.452	1.344	1.331	1.467	1.339	1.467	0.098	
	1.469	1.336	1.478	1.326	1.329	1.479	1.335	1.471	0.143	
	1.472	1.335	1.478	1.325	1.329	1.483	1.324	1.528	0.162	

For tetramer (HF) and hexamer (HF) of OCNCY only the bond lengths for the central monomer are included since they are the same for all central units.

Table 5
Bond lengths (in Å) and excitation energies for dicyanomethylene fulvene oligomers (OCNFv)

Oligomer/method	α'-β'	β'-β	β-α	Intra-cell	Inter-cell	α_1-β_1	β_1-β'_1	β'_1-α'_1	δ_r	E_{cal} (eV)
Monomer (HF)	1.525	1.326	1.487	1.337		1.487	1.326	1.525		8.26
Monomer (CIS)	1.512	1.359	1.451	1.391		1.451	1.359	1.512		3.47
Dimer (HF)	1.523	1.325	1.490	1.340	1.348	1.471	1.332	1.475	0.154	6.57
	1.475	1.332	1.471	1.340	1.348	1.490	1.325	1.523	0.154	
Dimer (CIS)	1.522	1.328	1.481	1.359	1.405	1.445	1.376	1.412	0.098	2.35
	1.412	1.376	1.445	1.359	1.405	1.481	1.328	1.522	0.098	
Tetramer (HF)	1.474	1.330	1.474	1.344	1.348	1.475	1.330	1.473	0.136	6.05
Tetramer (CIS)	1.523	1.325	1.490	1.340	1.348	1.470	1.332	1.476	0.154	2.34
	1.473	1.330	1.475	1.345	1.348	1.474	1.330	1.473	0.134	
	1.473	1.332	1.467	1.362	1.406	1.449	1.374	1.410	0.088	
	1.411	1.377	1.443	1.360	1.406	1.480	1.328	1.521	0.096	
Hexamer (HF)	1.474	1.330	1.474	1.344	1.348	1.475	1.330	1.473	0.136	5.94
Hexamer (CIS)	1.523	1.325	1.490	1.340	1.348	1.470	1.332	1.475	0.154	2.32
	1.473	1.330	1.475	1.345	1.348	1.473	1.330	1.473	0.134	
	1.472	1.333	1.465	1.364	1.407	1.447	1.375	1.410	0.079	
	1.410	1.375	1.446	1.364	1.348	1.465	1.333	1.472	0.093	
	1.473	1.330	1.473	1.345	1.348	1.475	1.330	1.473	0.134	
	1.475	1.332	1.470	1.340	1.348	1.490	1.335	1.523	0.151	

For tetramer (HF) and hexamer (HF) of OCNFv, only the bond lengths for the central monomer are included since they are the same for all central units.

From Table 1, it is clear (and consistent with previous findings) that relative to CIS results, excitation energies obtained with the use of the Koopman's theorem [6] from RHF calculations are much too large by a factor of almost two and local DFT (LSDA) values are much too small again by a factor of two. There are very few experimental results for cyclopentadiene and fulvene oligomers. For *aromatic* cyclopentadiene and fulvene monomers, the lowest $\pi - \pi^*$ optically allowed transitions have been reported to be located at about 5.3 eV [25,16]. Hence direct comparison with our systems is not possible. Given our previous calibrations [5], it appears that CIS excitation energies slightly overestimate experimental values by 0.1–0.3 eV. For comparison purposes, we also included the vertical excitation values (denoted by 1SCF in Table 1) for some monomers and dimers. The differences between 1SCF and optimized values are of the order of 1 eV. The lowering of energy is largely due to geometry relaxation observed in the optimized structures and will be discussed below. In one case (dimers), we considered the effect of basis sets on the

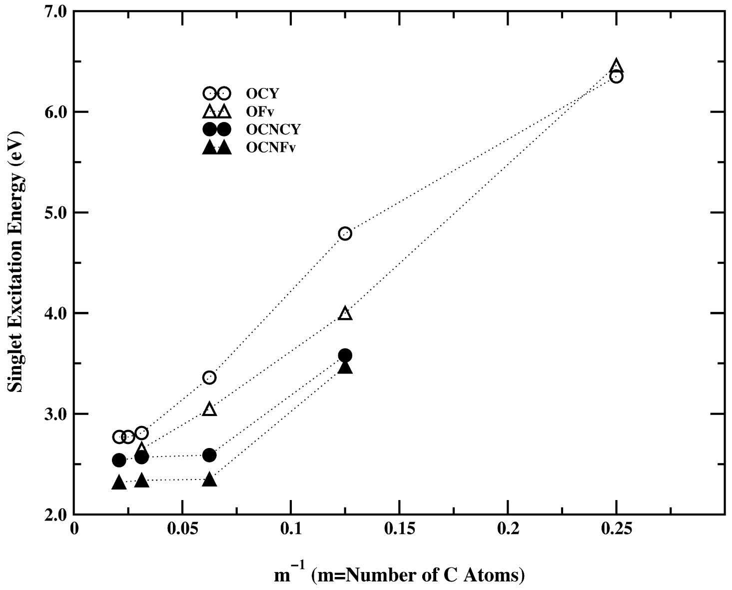


Fig. 3. CIS excitation energies plotted as a function of inverse chain length (m^{-1}, where m is the number of atoms along the chain backbone) for oligomers as indicated on the figure.

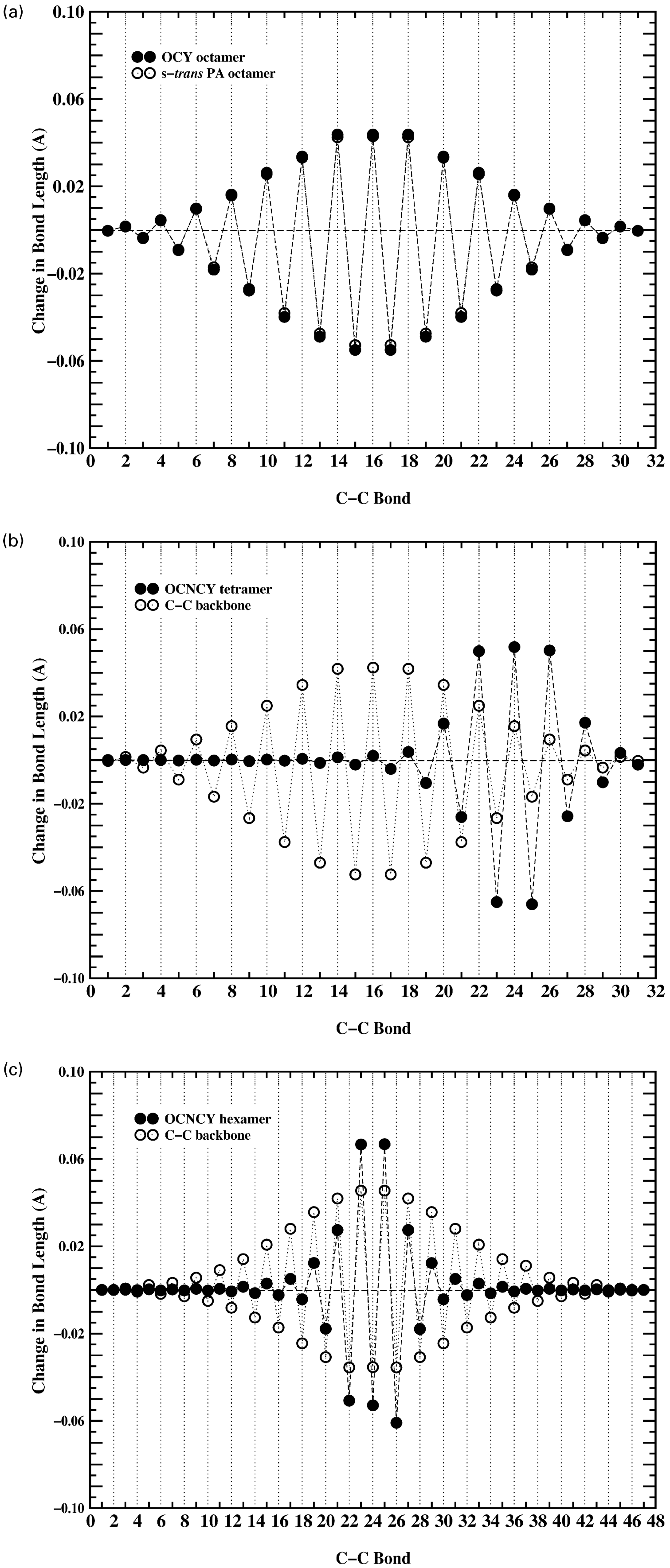


Fig. 4. Bond length differences between the HF and CIS values shown for: (a) octamer of OCY; (b) tetramer of OCNCY; (c) hexamer of OCNCY. The corresponding *s-trans* OA backbone is also shown for comparison in (a)–(c).

excitation energies. The excitation energies were lowered by approximately 0.1 eV when 6-31G* basis set was used instead of 3-21G*.

In Fig. 3, we plotted the optimized excitation energies as function of the inverse of chain length. In all four cases, CIS results do not extrapolate linearly to the infinite chain band gap value, rather they seem to saturate at certain values (2.8 eV for OCY, 2.6 eV for OFv, 2.5 eV for OCNCY and 2.3 eV for OCNFv). The saturation point is often related to the effective length or the mean conjugation length of polymers [26]. Table 1 and Fig. 3 indicate that the mean effective length for PCY and PFv is around eight monomers and for PCNCY and PCNFv, it is around four monomers.

3.2. Ground state (HF) geometries

For all systems, except for the hydrogen atoms attached to the sp_3 carbons, the chains have planar geometry.

OCY. Table 2 summarizes the ground state (HF) bond lengths of the OCY. In the longer oligomers (e.g. octamer), ignoring the end effects, the respective bond lengths are the same in the central part. Hence it can be concluded that for polymers, we would have 1.467 Å for $C_{\alpha'}-C_{\beta'}$ and $C_{\beta'}-C_{\alpha}$, 1.334 Å for $C_{\beta'}-C_{\beta}$, and 1.326 Å for intra- and inter-cell distances. The δ_r values for quinonoid OCY are found to be 0.17 and 0.14 Å for the dimer and the octamer, respectively.

OFv. The optimized (HF) bond lengths for OFv are presented in Table 3. In longer oligomers (e.g. octamer), the central respective bond lengths have the same values. Hence for polymers, we would predict that $C_{\alpha'}-C_{\beta'}$ and $C_{\beta}-C_{\alpha}$ would be 1.466 Å, $C_{\beta'}-C_{\beta}$ 1.326 Å and intra- and inter-cell distances are 1.350 Å. These values are very similar to the ones in OCY with the exception that in OFv, the intra- and inter-cell distances are slightly longer (by 0.02 Å). For quinonoid OFv the δ_r values range between 0.16 Å (for dimer) and 0.13 Å (for octamer), which shows a weak transformation towards more aromatic form relative to OCY.

OCNCY. The geometric parameters for the quinonoid OCNCY oligomers are given in Table 4. For the longer oligomer such as hexamer, in the central part, we obtain 1.471 Å for $C_{\alpha'}-C_{\beta'}$ and $C_{\beta'_1}-C_{\alpha'_1}$, 1.335 Å for $C_{\beta'}-C_{\beta}$ and $C_{\beta_1}-C_{\beta'_1}$, 1.480 Å for $C_{\beta}-C_{\alpha}$ and $C_{\beta_1}-C_{\alpha_1}$, and 1.326 and 1.329 Å for intra- and inter-cell distances, respectively. The δ_r values for quinonoid PCNCY oligomers range from 0.16 Å (end-rings) to 0.14 Å (central-part). Since δ_r values for OCY and OCNCY are nearly the same, it can be concluded that the addition of cyano group in OCY does not change its ground state backbone structure significantly.

OCNFv. The HF optimized bond lengths of the quinonoid OCNFv are given in Table 5. For the longer hexamer, we obtain 1.473 Å for $C_{\alpha'}-C_{\beta'}$, $C_{\beta'_1}-C_{\alpha'_1}$, $C_{\beta}-C_{\alpha}$ and $C_{\beta_1}-C_{\alpha_1}$, 1.330 Å for $C_{\beta'}-C_{\beta}$ and $C_{\beta_1}-C_{\beta'_1}$, and 1.344 and 1.348 Å for intra- and inter-cell distances, respectively. The average bond length alternations as given by δ_r values are 0.15 Å (end-rings) or 0.14 Å (central part). Again illustrating that the inclusion of cyano group in OFv in its ground state does not change the geometry of its backbone significantly.

3.3. Excited state (CIS) geometries

In all cases considered, we observe geometry relaxation phenomena in the optimized excited state structures. The carbon–carbon single and double bonds are altered considerably inside the oligomers, the C–C bonds are shortened while the C=C bonds are elongated with respect to their ground state values. In the center of charge delocalization, nearly benzenoid-like geometry is obtained (i.e. the inter- and intra-ring carbon–carbon bond lengths are becoming almost equal). The actual values for the bond lengths are given in Tables 2–5 for OCY, OFv, OCNCY and OCNFv. The easiest way to observe what is happening to their geometries is to consider the bond length alternation values in the excited states. Considering the longest oligomers in each case, we note that δ_r values range from 0.17 to 0.04 Å for OCY, from 0.16 to 0.04 Å for OFv, from 0.16 to 0.09 Å for OCNCY and from 0.15 to 0.08 Å for OCNFv. It can be concluded that, when end effects are ignored, the bond length differences decrease more in OCY and OFv than in OCNCY and OCNFv in their respective excited states. However, it is also evident that similar to their ground states, there are structural similarities between OCY and OFv, and OCNCY and OCNFv. This is further supported by the similarities between their excitation energies (we obtained 2.7 and 2.8 eV for OCY and OFv octamers, and 2.5 and 2.3 eV for OCNCY and OCNFv hexamers, respectively). To summarize, the excited state geometries of OCNCY and OCNFV, where the dicyanomethylene group is inserted between the two cyclopentadiene and fulvene rings, respectively, show small changes with respect to the excited state geometries of their parent oliogmers (OCY and OFV).

3.4. Geometry relaxation phenomena

Geometry relaxation phenomena play a very important role in the changeover from one type of oligomer configuration to another (quinonoid $\rightleftharpoons$ aromatic). This is phenomena has been observed previously, for example see reference [19] (and references within). As expected, we find that, for all the molecules, a strong relaxation does indeed take place in their excited states, i.e. the geometry which is found to be optimal for their ground states does not constitute the optimal geometry in the lowest excited states. The equilibrium structural parameters have been discussed above. In this section, we display the structural deformations on Figs. 4 and 5 where we plot the differences between the HF and CIS bond lengths for OCY and OFv octamers, and for OCNCY and OCNFv tetramers and hexamers. For comparison we also include the differences between the HF and CIS bond lengths for *s-trans* OA.

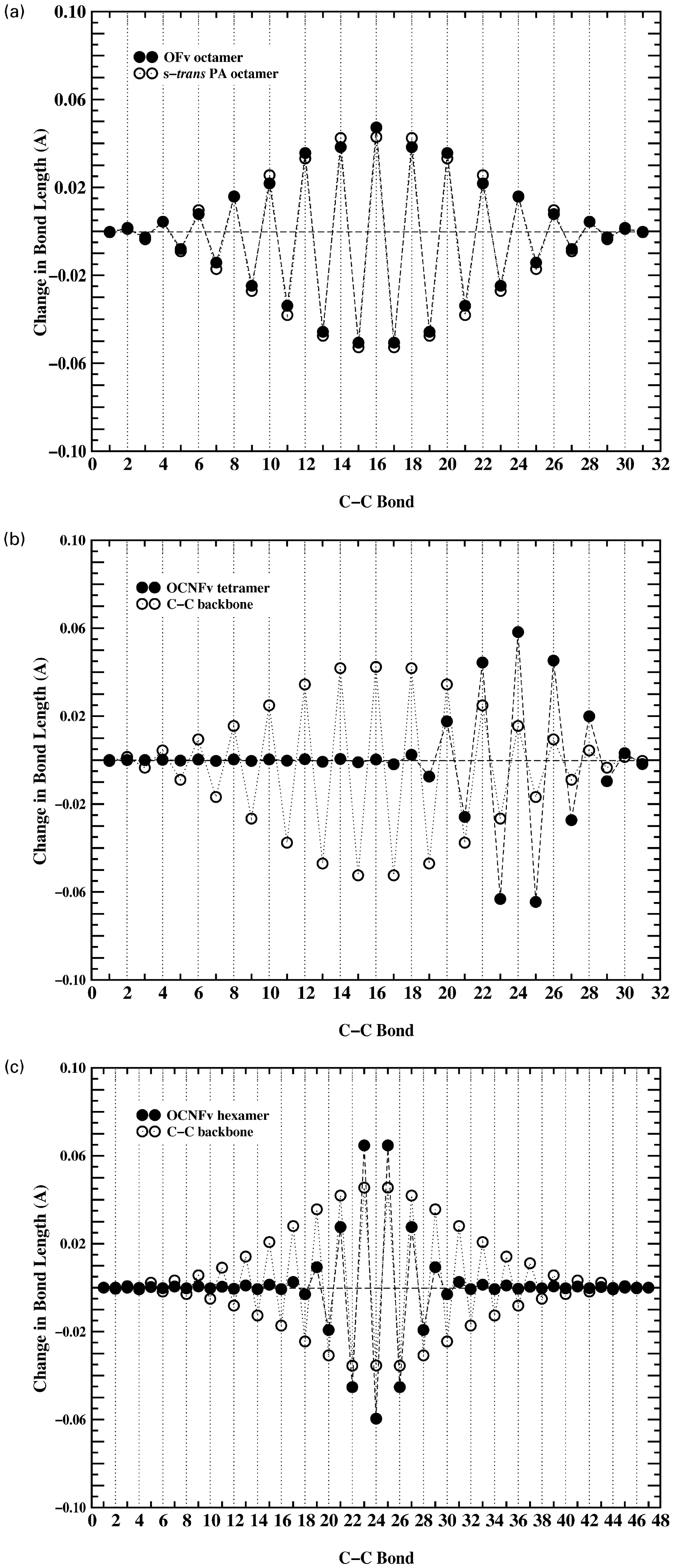


Fig. 5. Bond length differences between the HF and CIS values shown for: (a) octamer of OFv; (b) tetramer of OCNFv; (c) hexamer of OCNFv. The corresponding *s-trans* OA backbone is also shown for comparison in (a)–(c).

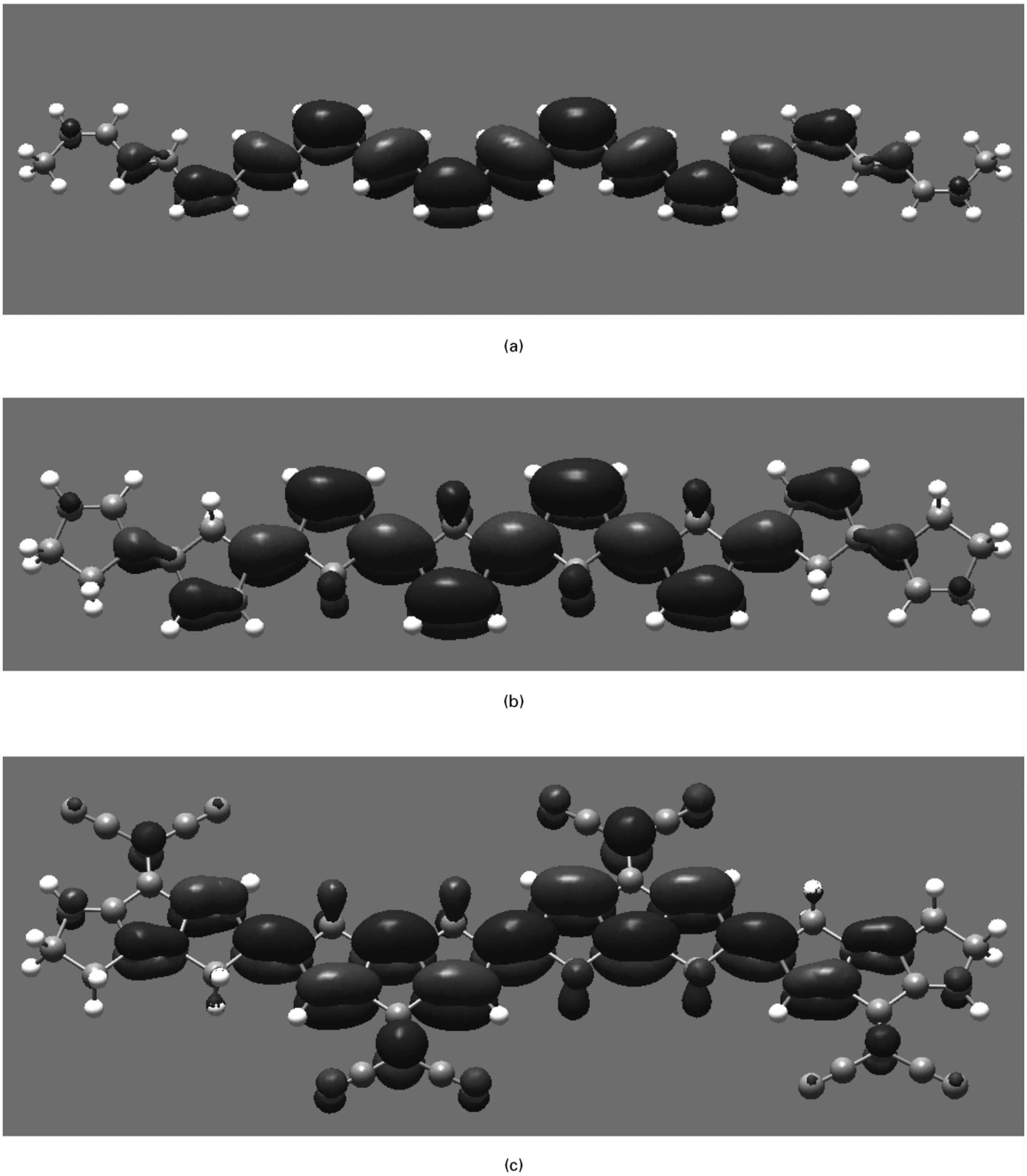


Fig. 6. Schematic representation of the HOMO for (a) *s-trans* acetylene octamer; (b) OCY (octamer); (c) OCNCY (tetramer).

Figs. 4(a) and 5(a) illustrate that CIS optimized geometries show considerable deformations in the central portions of the in OCY and OFv. These deformations spread over approximately six rings and they closely match a similar deformation observed in *s-trans* OA. The geometric deformations taking place in the excited states of cyano-substituted oligomers, OCNCY and OCNFv, are not located centrally for tetramers (see Figs. 4(b) and 5(b)). The relaxations are more localized and spread over approximately three rings (~ one monomer). This should be contrasted with unsubstituted C–C backbone included in these figures which has a similar shape to the one

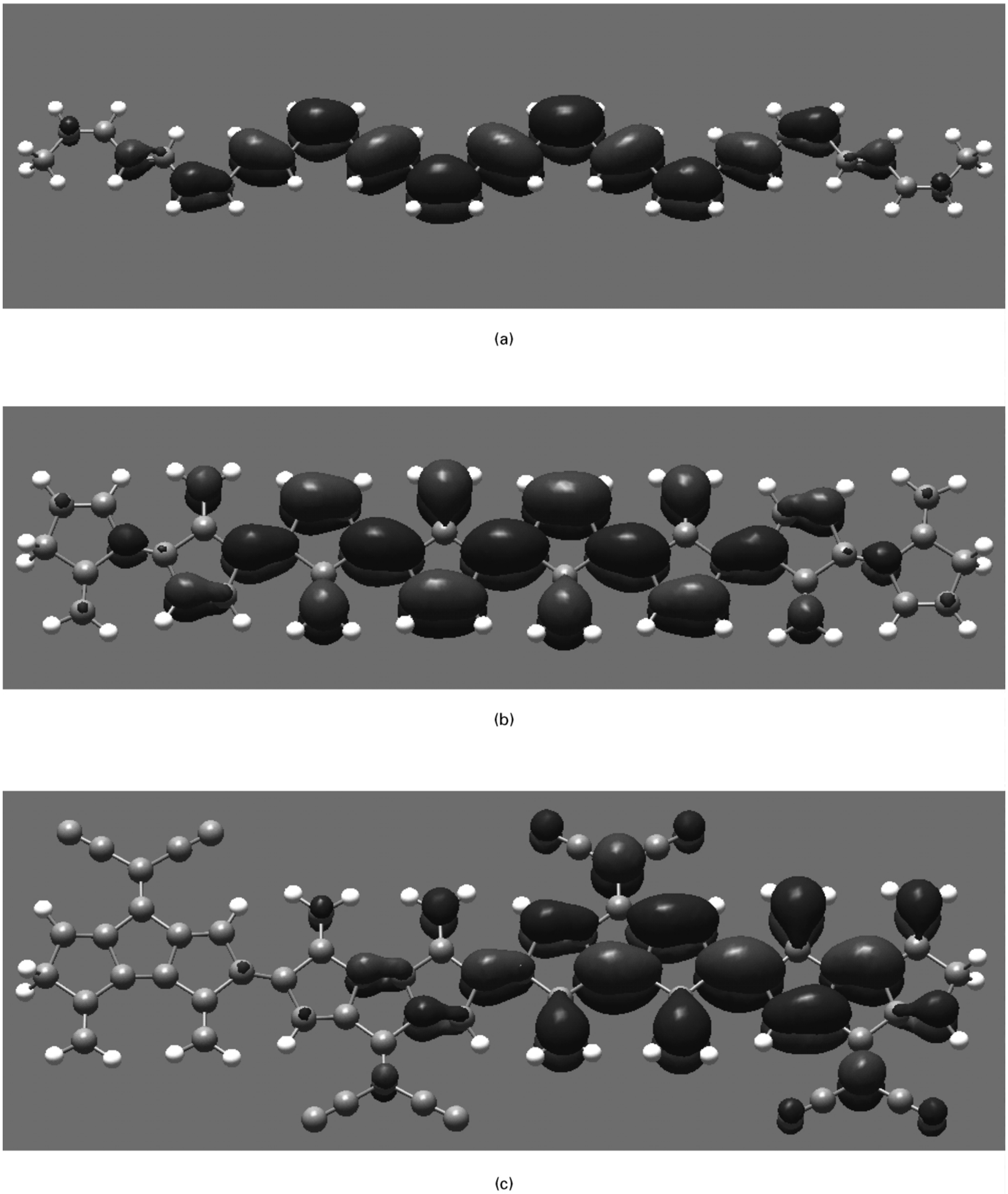


Fig. 7. Schematic representation of the HOMO for (a) *s-trans* acetylene octamer; (b) OFv (octamer); (c) OCNFv (tetramer).

observed for OCY and OFv. For hexamers of OCNCY and OCNFv, the deformations become central again (see Figs. 4(c) and 5(c)) however, they remain highly localized over three instead of six rings as observed in OCY and OFv. The geometry modifications in the outer rings (i.e. outside the central deformation) are much weaker, essentially adopting a geometry equivalent to that of the HF ground state.

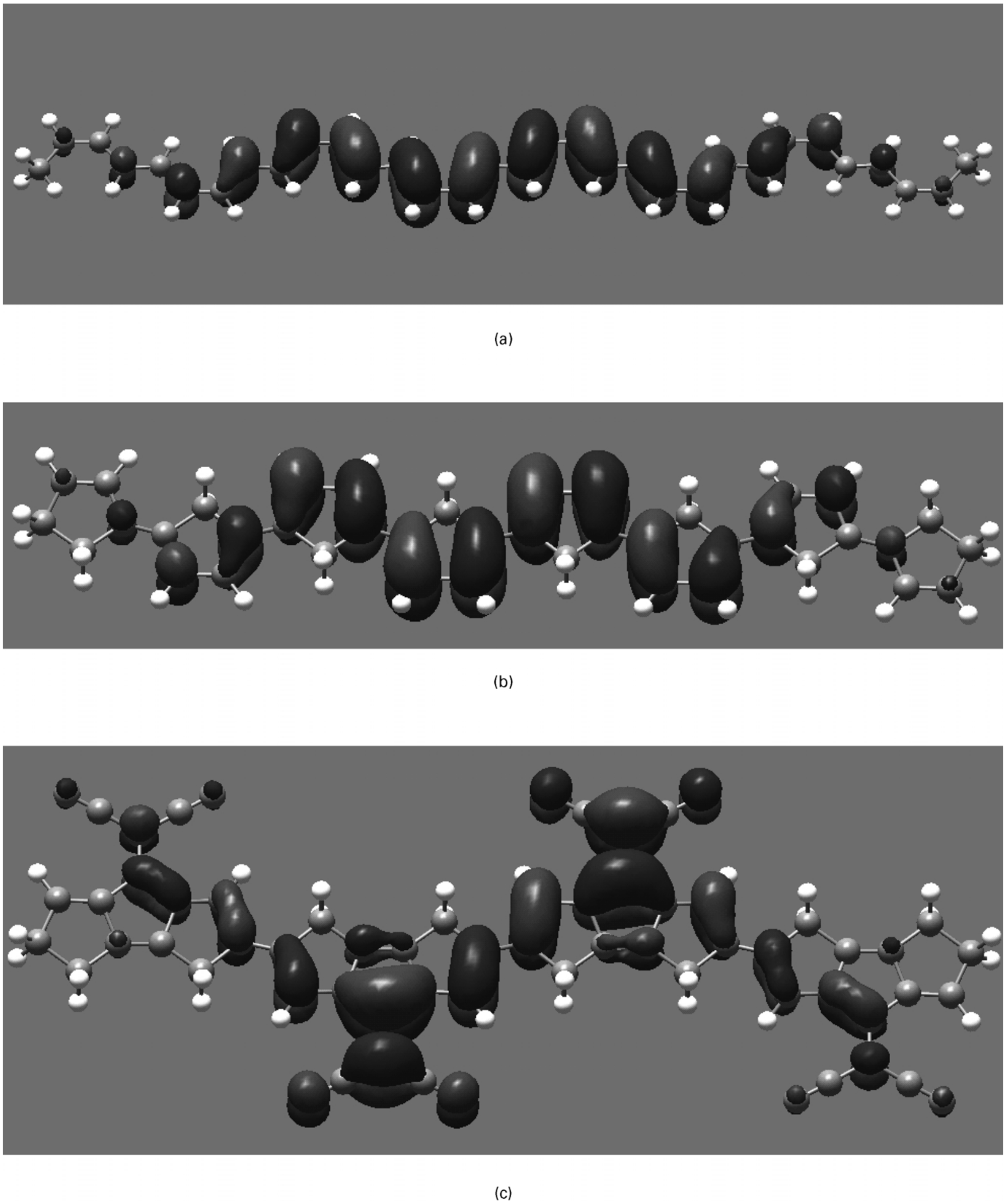


Fig. 8. Schematic representation of the LUMO for (a) *s-trans* acetylene octamer; (b) OCY (octamer); (c) OCNCY (tetramer).

3.5. Molecular orbital analysis

All oligomers studied in this work have near C_{2h} symmetry. All bonding one electron orbitals are doubly occupied, so the symmetry of the ground state, S_0, is A_g. The promotion of one electron from HOMO to LUMO generates an excited state of symmetry B_u. Transitions between a_g and b_u is dipole allowed. The CIS calculations show that the

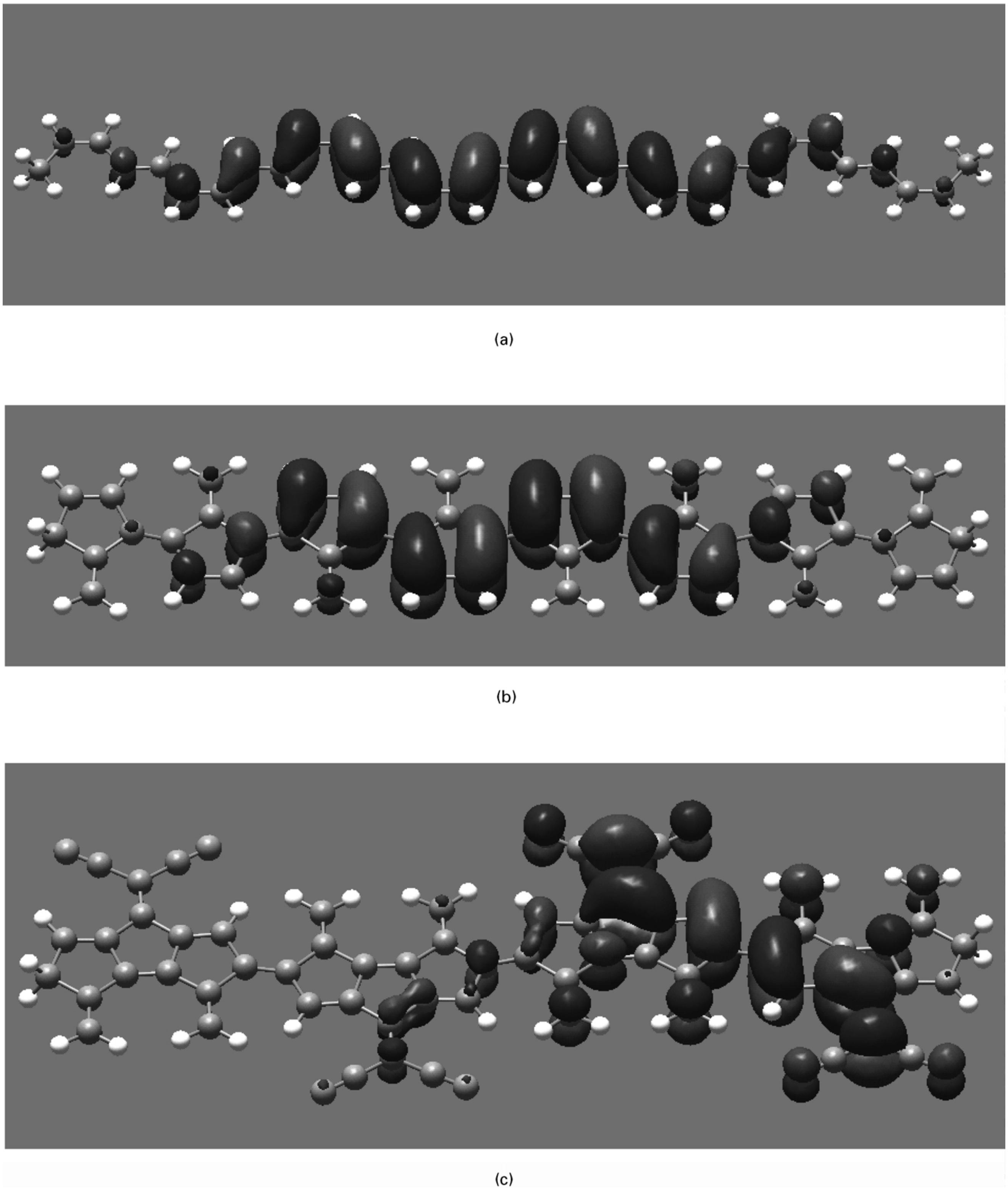


Fig. 9. Schematic representation of the LUMO for (a) *s-trans* acetylene octamer; (b) OFv (octamer); (c) OCNFv (tetramer).

lowest singlet excited states correspond predominantly to a transition between the HOMO and the LUMO level. The coefficient of CI expansions corresponding to these transitions are approximately 0.6. Other single excitations, that contribute to the total excited state wavefunction, involve transitions between HOMO-1 and HOMO-2 to LUMO + 1 and LUMO + 2 levels. In order to gain a better understanding of the geometry deformation discussed above and as an example of the molecular orbital trends, we plot the HOMOs and LUMOs for compounds studied in Figs. 6–9 [27] for backbones consisting of the same number of atoms (otamers for OCY and OFv and tetramers for OCNCY and OCNFv). It is clear from these figures that lowest occupied states are not affected very much by the presence of CH_2 or $C{=}CH_2$ and then by the inclusion of cyano bridging group. Especially the HOMO remains basically unaltered as one goes from OA backbone to OCY and then to OCNCY. There is a bit more difference between OA backbone and OFv and OCNFv. In the case of OCNFv the MOs become localized at one or the other end of the molecule. There results correlate with the fact that HOMO eigenvalues are not changed very much by an introduction of CH_2 or $C{=}CH_2$ and/or cyano group into the parent oligomers. All three compounds clearly display the quinonoid structure with double bonds along the $\beta'-\beta$ and/or $\beta_1 - \beta_1'$ bonds in the rings.

LUMO is especially important because as stated above, in the excited state this orbital becomes the lowest orbital that is most likely to be occupied by an excited electron. From Fig. 8, one notes that the LUMOs of OA, OCY are quite similar. The LUMO of OCNCY extends more laterally instead of along the backbone. Similarly, from Fig. 9 one observes that while LUMOs of OA and OFv are nearly the same, the LUMO of OCNFv again extends more laterally (and asymmetrically) instead of along the backbone. Our calculations show that the lowering of excitation energy between OCY and OCNCY, and OFv and OCNFv is largely due to the lowering of the LUMO in OCNCY and OCNFv relative to the LUMOs of OCY and OFv, respectively. The aromatic structure of the LUMO (and LUMO + 1 and LUMO + 2, etc. not shown) explains why the geometry of the singlet excited states becomes more benzenoid-like in the central part of the oligomer.

4. Conclusions

The optimized equilibrium geometrical parameters for all oligomers obtained using both the HF and CIS methods are given in Tables 2–5. As can be seen from δ_r values, geometry relaxation phenomena play an important role in excited state geometries of OCY, OFv, OCNCY and OCNFv. The bond length alternation decreases from approximately 0.14 Å in S_0 to 0.04 Å in S_1 state of octamers, OCY and OFv, and to 0.09 Å in S_1 state of hexamers, OCNCY and OCNFv. In effect, a change occurs from one kind of isomer to another (quinonoid → aromatic). The lattice distortion extends over approximately six rings in OCY and OFv and three rings in hexamers of OCNCY and OCNFv (Figs. 4 and 5). From the molecular orbital analysis, we note that the highest occupied and lowest unoccupied MOs are more localized in cyano-derivatives in comparison to their parent oligomers of equivalent lengths (Figs. 6–9). The trends in the lowest singlet excitation energies for OCY, OFv, OCNCY, and OCNFv indicate that the band gap lowering in OCNCY and OCNFv relative to their parent oligomers would be small (less than 0.5 eV) and hence PCNCY and PCNFv would not produce small intrinsic band gaps comparable to the one observed in PCNTH (0.8 eV). In fact, based on our results we predict that band gaps for PCNCY and PCNFv would be of the order of 2 eV (similar to their parent polymers) in agreement with some previous findings [20,22,21].

Acknowledgements

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