Theoretical Investigation of the Charge Injection Effects on the Electronic Properties of Substituted Oligodiacetylenes

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We discuss the charge-induced modifications in the ground state geometry and in the electronic properties of two types of fully carbazolyl-substituted oligodiacetylenes, named CBD_n and CHD_n respectively, which are taken as models of the corresponding polymers. Quantum chemical calculations have been performed on the isolated oligomers carrying substituents, either directly linked to the backbone (CBD_n) or connected to it through a methylene spacer (CHD_n). The collective electronic oscillator (CEO) approach is used to compute the excitations in terms of the one-electron transition density matrixes (CEO-modes). The simulated photoinduced absorption spectra which are obtained show interesting features, and the allowed low-energy transitions compare favorably with experimental results where available. Two-dimensional plots in real space of the CEO-modes allow us to analyze the physical nature of the excitons in terms of the photoinduced electron/hole pairs motion. For charged oligomers, two different types of electronic interactions between the π systems of the backbone and of the substituents are seen to occur in the two types of oligomers. Even in the presence of a methylene spacer, a charge flow is unexpectedly observed from the backbone toward the carbazolyl substituents, and a manifold of allowed low-energy excitations rises. In this way, the experimental peaks in the photoinduced absorption spectra of polyDCHD (the polymer corresponding to CHD_n) find a new explanation, which is different from (and more convincing than) that previously given by us on the basis of results obtained on unsubstituted oligomers.

1. Introduction

Organic conjugated materials have achieved increasing importance in the development of new devices for a wide variety of technological applications,[1] e.g., organic light emitting diodes (LED's),[2,3] light emitting electrochemical cells and solar cells,[4] photodiodes,[5] or field effect transistors (FET).[6] The photo- and physicochemical properties of these materials, whose knowledge is fundamental for the development of devices, are very complex due to the many types of processes involved. For example, photoexcitation could occur through different types of channels involving, e.g., singlet or triplet excitons or charge-separation states, and on the other hand charge transport and recombination processes are strictly correlated to the stability of the charge-induced geometry relaxation. Knowledge of these processes is important for understanding the mobility of the charge induced defects and their recombination in real devices such as LEDs[7] or (as recently demonstrated) electrochemical actuators.[8]

This complexity forms an interesting subject for theoretical investigation trying to understand the relationships between the molecular geometry and the electronic properties, to help in developing new conjugated materials showing improved technological properties. For these reasons, a wide number of theoretical and experimental studies has been dedicated to this matter. Due, however, to the large computational size of the systems involved, most theoretical work is focused on unsubstituted oligomers or polymers. This implies neglecting the possible interactions between the π system of the backbone and the substituents, either because they are implicitly assumed to be small or because the lower excitations of the substituted systems are believed to essentially belong to the π system of the backbone. On the other hand, experiments are frequently carried out on substituted systems, which can render the comparison with the theoretical results often questionable.

What we want to do here is to contribute to throw light on these problems, taking advantage of the opportunities given by a recent theoretical approach, the CEO method,[9,10] to study the electronic properties of fairly large substituted systems in a way which explicitly takes into account the possible interactions between the conjugated backbone and the substituents. We consider doubly positive photoexcitons induced by charge injection on oligomers of a particular class of polydiacetylenes that are interesting materials for their large off-resonance optical nonlinearities and as models of rodlike systems.[11,12] The general formula of the carbazolyl-substituted oligodiacetylenes studied is given in Figure 1. When the chromophore groups are directly linked to the backbone, we have the *n*-oligomer of the 1,4-bis-(N-carbazolyl)-1,3-butadiyne (named CBD_n), whereas when a methylene spacer is present, we have the *n*-oligomer of the 1,6-bis(N-carbazolyl)-2,4-hexadiyne (named CHD_n). Polycarbazolyldiacetylenes of these and other types have been long characterized and studied in our laboratory.[13] In the following, *n* takes the values 2, 4, and 6.

2. Theory and Computational Details

The electronic excitations have been computed using the collective electronic oscillator (CEO) method on the basis of the AM1[14] optimized ground-state geometries obtained using the MOPAC[15] code. The AM1 Hamiltonian is known to be well suited to reproduce with good accuracy the ground-state geometries of large-sized organic systems.[16]

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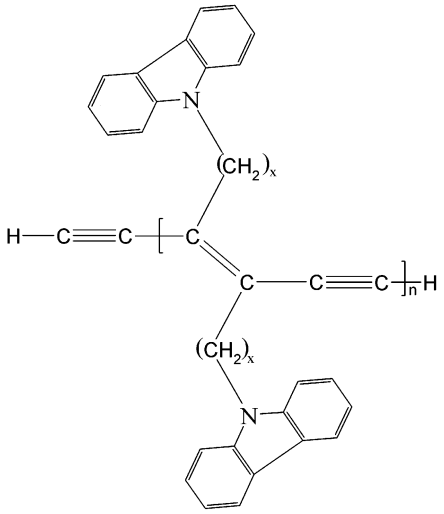


Figure 1. Molecular structure of the CBD_n ($x = 0$) and CHD_n ($x = 1$) oligomers.

The CEO technique[17] was developed in the time-dependent Hartree−Fock (TDHF) framework, in which it is assumed that the many-electron wavefunction $\Psi(t)$, describing the molecular system when perturbed by an external time-dependent field, is represented at all times by a single Slater determinant. In this approach, however, one does not directly seek the excited electronic wavefunctions but only the one-electron transition density matrixes,[17,18] which are named the electronic modes ξ_a (to which correspond the excitation energies Ω_a). This choice allows us to sensibly increase the dimension of the basis set that can be used in the calculations and, consequently, the size of the chemical system which can be studied. Knowledge of the ordered pairs (Ω_a,ξ_a) is all we need for the evaluation of the linear optical response through the calculation of the dynamic polarizability $\alpha(\omega)$[17,18]

$$\alpha(\omega) = \sum_a \alpha_a(\omega) = \frac{2}{3}\sum_a \frac{\Omega_a Tr(\vec{\mu}\xi_a)^* \, Tr(\vec{\mu}\xi_a)}{\Omega_a{}^2 - (\omega + i\Gamma_a)^2} \quad (2.1)$$

where Γ_a is the dephasing rate for the excited state a.

The optimized ground state geometries of the neutral and doubly positively charged oligomers, obtained using the MOPAC code without any symmetry constraint, are used as an input for the CEO code developed by the Mukamel's group,[19] where the CEO procedure is implemented on the basis of a semiempirical INDO/S Hamiltonian.[20] [At present we consider only doubly charged systems because we are using a restricted Hartree−Fock procedure.] The original parameters of the INDO Hamiltonian[21] were reoptimized by the Zerner's group in order to reproduce the electronic spectra of organic molecules.[22] In eq 2.1, the number of modes considered has been 60 for the neutral and 80 for the charged oligomers and the corresponding oscillator strengths have been also computed according to the expression $f_a = (2/3)\Omega_a Tr(\vec{\mu}\xi_a)^* \, Tr(\vec{\mu}\xi_a)$. The optical spectrum $\mathcal{J}(\omega)$ has been obtained through the expression

$$\mathcal{J}(\omega) \propto \sum_a \mathrm{Im}[\alpha_a(\omega)] \quad (2.2)$$

where a common value of 0.03 eV is assumed for all the dephasing rate coefficients (Γ_a).

The plots of the calculated one-electron transition density matrixes ξ_a contracted over the atoms, that is, in the real space, give a representation of the electron−hole pairs motions induced by the photon absorption during the excitation process. This allows us to correlate the electron density variations with the optical and topological properties of the molecular systems studied and can give information on the molecular design of new structures. In the two-dimensional plots, where the x (y) axis represents electrons (holes) on an atom, diagonal elements $(\xi_a)_{rr}$ are related to the net photoinduced charge on the rth atom, while the off-diagonal element $(\xi_a)_{rs}$ represents the probability of finding an electron and a hole on the rth and sth atom, respectively. So the difference between the values of two symmetrical off-diagonal elements gives information about the probability and the direction of charge transfer between the rth and sth atom.

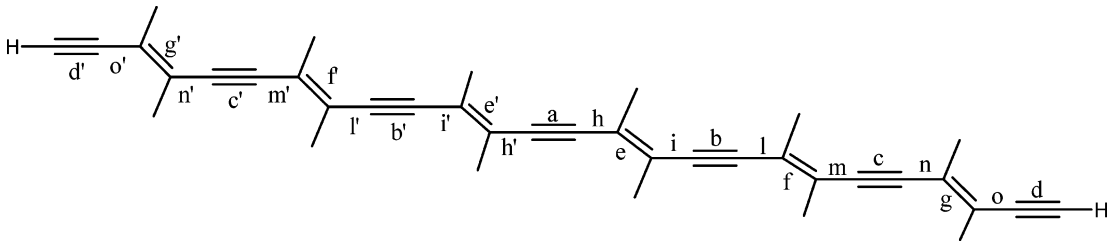
3 Results and Discussion

3.1. Geometries and Charge Distributions. The AM1 bond lengths, computed without forcing any symmetry constraint, for the neutral and charged oligomers are shown in Tables 1 and 2 for the backbone and carbazolyl moieties, respectively. The reported carbazolyl bond lengths are mean values over n and over all the substituents belonging to a given oligomer, the overall standard deviation being less than ±0.001 Å.

In the neutral case, only the backbone bond lengths for the largest oligomers considered ($n = 6$) are reported, because no particular variations occur with increasing n. In CHD_6, the triple bonds are longer than in CBD_6, whereas the opposite occurs for double and single bonds. From Table 2, it is seen that in the two types of neutral oligomers the geometries of the carbazolyl moieties are very close to each other, with the only exception of the bonds springing from the N atoms. Of these, the bonds directly involved in the carbazolyl π system (labeled h in the Table) are longer in CBD_6 (by 0.014 Å), and the reverse is true (by −0.015 Å) for the bond, labeled i, connecting the substituent to the backbone. With the AM1 bond lengths for isolated C≡C, C═C, and C−C being 1.195, 1.339, and 1.536 Å, respectively, the results in Table 1 indicate that for CBD_n two somewhat concurrent conjugation pathways are effective. The first one runs over the whole π system of the backbone, whereas the second includes two neighbor carbazolyl moieties connected by a backbone double bond. For CHD_n, a comparison with the bond lengths of the unsubstituted oligomer[23] (1.202 Å for C≡C, 1.350 Å for C═C and 1.402 Å for C−C) shows that the presence of the spacer almost prevents any *direct* interaction between the two moieties. The computed values compare favorably (especially for CHD_n) with the experimental backbone structure of a similarly substituted polydiacetylene[24] (1.21, 1.36, and 1.41 Å for the triple, double, and single CC bonds, respectively). Finally a last point deserves mention. Although not reported in the table, strong variations (50÷75°) are obtained for the backbone dihedral angles with respect to the ideal values (180°) valid for the unsubstituted oligomer C_{2h} structure, due to the presence of the carbazolyl moieties. The largest deviations are found for CBD_n and in general near the chain ends. Increasing the oligomer size seems to slightly reduce these variations, an effect that can be expected to continue for larger oligomers ($n \gg 6$) due to the backbone conjugation. In this respect, it is important to stress that, despite the nonplanar backbone structure, in both CBD_n and CHD_n the presence in the triple bonds of *two orthogonal* π bonds allows a considerable extent of conjugation with the π electrons of the neighbor double bonds.

For doubly charged oligomers, the bond length differences are enhanced, and a number of somewhat unexpected features emerge. First, for CHD_n, the backbone bond lengths are

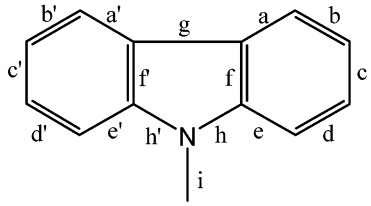
TABLE 1: Backbone Bond Lengths (Å) for Neutral and Doubly Charged CBD_n and CHD_n Oligomers



		triple bonds[a]				double bonds[a]			single bonds[a]					
		a	b b′	c c′	d d′	e e′	f f′	g g′	h h′	i i′	l l′	m m′	n n′	o o′
							Neutral							
CBD_6		1.199	1.199	1.199	1.197	1.380	1.380	1.380	1.417	1.417	1.417	1.417	1.417	1.417
CHD_6		1.202	1.202	1.202	1.198	1.361	1.361	1.361	1.404	1.404	1.404	1.405	1.404	1.407
							1.364	1.359						
							Charged							
	n													
CBD_n	2	1.252	1.202			1.512			1.334	1.409				
						1.509								
	4	1.250	1.216	1.200		1.515	1.407		1.338	1.384	1.396	1.415		
			1.213			1.503	1.402		1.334	1.389	1.401			
	6	1.219	1.251	1.200	1.200	1.513	1.509	1.392	1.384	1.336	1.332	1.397	1.409	1.414
			1.204	1.210		1.414	1.386	1.382	1.392	1.408	1.417	1.414	1.419	1.417
CHD_n	2	1.203	1.200			1.359			1.403	1.404				
	4	1.202	1.202	1.199		1.362	1.359		1.404	1.404	1.404	1.405		
	6	1.202	1.202	1.202	1.199	1.361	1.364	1.360	1.404	1.404	1.404	1.404	1.404	1.405
							1.359							

[a] When the lengths of the primed and unprimed bonds are within 0.002 Å of each other, only one value is reported.

TABLE 2: Mean Values of the Bond Lengths in Carbazolyl Moieties (Å) for Neutral and Doubly Charged CBD_n and CHD_n Oligomers



	neutral		charged		
			CBD_n		
	CBD_n	CHD_n	type A	type B	CHD_n
a[a]	1.386	1.387	1.387	1.381	1.383
b	1.396	1.394	1.397	1.404	1.401
c	1.397	1.399	1.396	1.391	1.397
d	1.395	1.393	1.396	1.404	1.395
e	1.396	1.399	1.395	1.389	1.401
f	1.444	1.447	1.445	1.442	1.450
g	1.454	1.451	1.454	1.457	1.454
h	1.426	1.412	1.427	1.450	1.407
i	1.415	1.430	1.418	1.350	1.430

[a] In all cases, $|x - x'| \leq 0.002$ Å.

practically independent of *n*, and moreover, they are unchanged with respect to the neutral case, and the same holds for the carbazolyl moieties. On the contrary, for CBD_n, relevant geometry changes are predicted, which can be compared with those in the unsubstituted charged oligomer,[23] where the most relaxed bond lengths are 1.254, 1.447, and 1.321 Å for the triple, double, and single CC bonds, respectively. In Table 1, the lengthening of the double bond is seen to be markedly enhanced with respect to the unsubstituted case, the largest value here obtained being as much as 1.515 Å. For $n = 2$ and 4, the most significant variations are located in the middle of the chain, and the geometry changes take the same form in both oligomers, which suggests that in these systems the charge-induced defect finds enough room already in the dimer. On the contrary, for the $n = 6$ oligomer, a sufficiently large one to allow for the localization of geometrical relaxations in different backbone positions, the defect markedly shifts toward *one* of the chain ends. This arrangement has been checked to correspond to the most energetically stable structure, corresponding probably to the largest possible conjugation pathway. Also for the carbazolyl moieties, significant differences are found with respect to the CHD_n case, and in fact, from Table 2, two types of structures (A and B) are seen to occur. The type-A geometry corresponds to that found in the neutral oligomer, whereas in structure B the mean (maxi mum) variation in bond lengths with respect to the latter amounts to 0.014 Å (0.065 Å). Structure B occurs in the two carbazolyl units near the most modified backbone region, the largest relaxation concerning the already-mentioned bonds h and i (see above). In particular, the nitrogen-backbone bond (named i in Table 2) strongly shortens, and the bonds named h appreciably lengthen, thus signaling an increased (decreased) delocalization of the nitrogen lone pair into the former (the latter) bond(s). All of these results indicate that charge injection induces a modification involving a limited region of the backbone (one repeating unit) and four carbazolyl groups adjacent to it, as shown in Figure 2. This structure contains an excess charge of as much as +1.45e and involves a butatrienic-like conjugation path. Finally, we note that the charge injection only slightly modifies (by 10÷15°) the dihedral angles toward planarity.

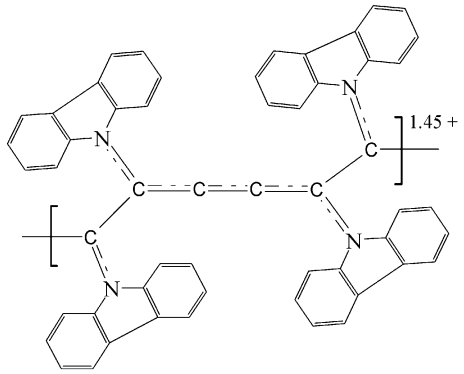


Figure 2. Schematic picture of the local charged induced structure in CBD_n oligomers.

TABLE 3: Charge Excess Distribution (%) in CBD_n and CHD_n Doubly Charged Oligomers

	CBD_n			CHD_n		
n	2	4	6	2	4	6
backbone	23.35	25.28	17.17	6.90	5.60	5.05
carbazole moieties (total)	76.65	74.72	82.83	93.10	94.40	94.95
I[a]	29.65	5.92	1.16	23.87	17.50	12.25
II	9.15	2.00	0.50	23.47	11.70	16.89
III	8.50	21.80	1.55	23.82	12.28	1.05
IV	29.35	4.50	1.96	21.94	8.30	0.10
V		7.90	6.25		4.70	3.20
VI		23.10	1.84		6.80	12.45
VII		2.35	23.00		14.85	1.85
VIII		7.15	7.64		18.30	11.38
IX			6.07			13.09
X			26.15			2.30
XI			2.28			14.45
XII			4.43			5.95

[a] For the numbering of carbazolyl units in the oligomers, see Figure 3.

In Table 3, the distribution of the excess charge among the backbone and the carbazolyl groups is displayed (see Figure 3 for the substituents numbering). For CHD_n, a very small fraction ($\leq$7%) of the excess charge is located on the backbone (a result which is confirmed by an ab initio RHF/6-31G optimization on CHD_2), and the rest is spread over all carbazolyl units, which explains the small geometry relaxations found in this type of oligomer. For CBD_n too, the fraction of charge on the backbone turns out to be small ($\leq$ 25%), and in both cases it basically decreases with increasing oligomer size. The relative positions of the INDO energies of the HOMOs of carbazole (−7.70 eV) and of the unsubstituted $n = 6$ oligomer (−6.88 eV) would suggest that it should be easier to extract an electron from the backbone. If, however, the calculations of the HOMO energies are performed at the actual geometries of the moieties in neutral CBD_6 (CHD_6), the results are −7.62 (−7.62) eV for carbazole and −8.73 (−8.27) eV for the backbones, due to the distortions mainly in the backbone dihedral angles caused by the carbazolyl interactions. The delocalization of an appreciable fraction of the excess charge on the backbone in CBD_n is only made possible by the already referred to conjugation effects involving the lone pairs of the N atoms. An analysis of the distribution of the excess charge among the carbazolyl groups shows that for CBD_n the majority of the charge is concentrated on the units belonging to the bipolaronic structure located toward one end of the chain, whereas for CHD_n, it is essentially equally distributed over the units at the chain ends. The latter results are consistent with those previously obtained by us[25] and by other authors[26] on unsubstituted oligodiacetylenes and oligophenylenes, respectively. It seems likely that in truly one-dimensional cases the bipolaron splits into two singlet polarons[27] only for extended π systems, whereas in the presence of carbazolyl substituents, the injected charge spreads over the latter moieties already for short oligomers. Otherwise, for CBD_n, which can be seen as a two-dimensional conjugated π system, the transverse conjugation stabilizes the bipolaron structure.

Finally in Figure 4, we report, as an example, a picture of the optimized structures for the neutral and doubly charged CBD_6 and CHD_6 oligomers. It seems likely that for charged CBD_6 the location of the charge-induced defect and its morphology remind the structure of cis 2-butene, and that for both oligomers the carbazolyl moieties assume a helical arrangement.

3.2. Excited States and Absorption Spectra. The theoretical absorption spectra, calculated as specified in section 2, are shown in Figure 5 for neutral oligomers, as well as in Figure 7 for the doubly charged ones. We remind that we are using a kind of restricted Hartree−Fock procedure, and consequently, only singlet excitations are obtained. Moreover, with the number

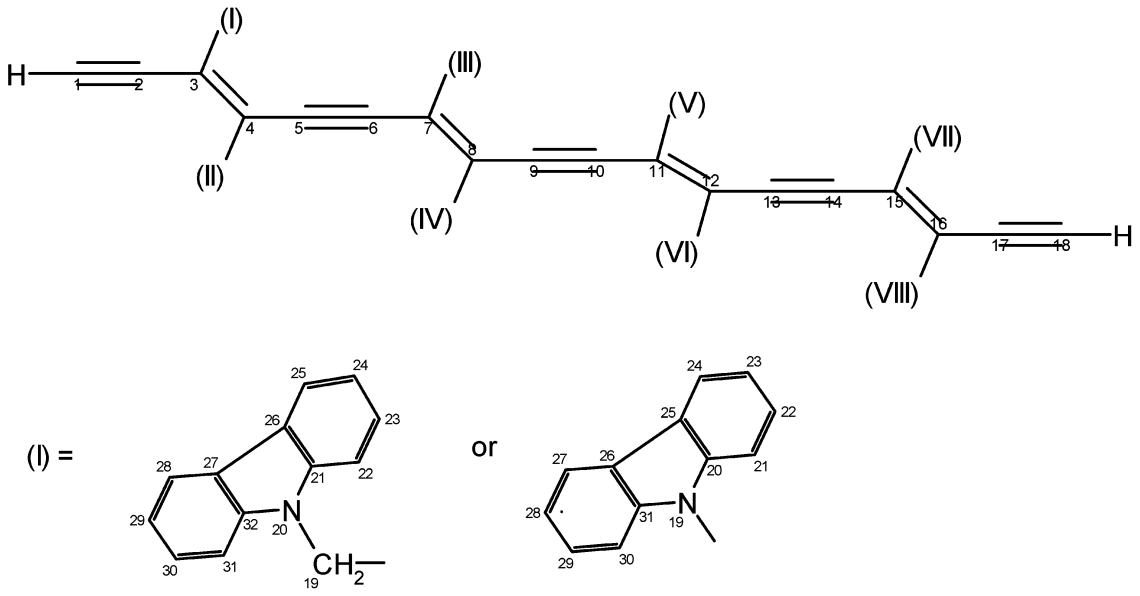


Figure 3. Atom numbering in the backbone and in the carbazolyl units in CHD_4 and CBD_4 oligomers.

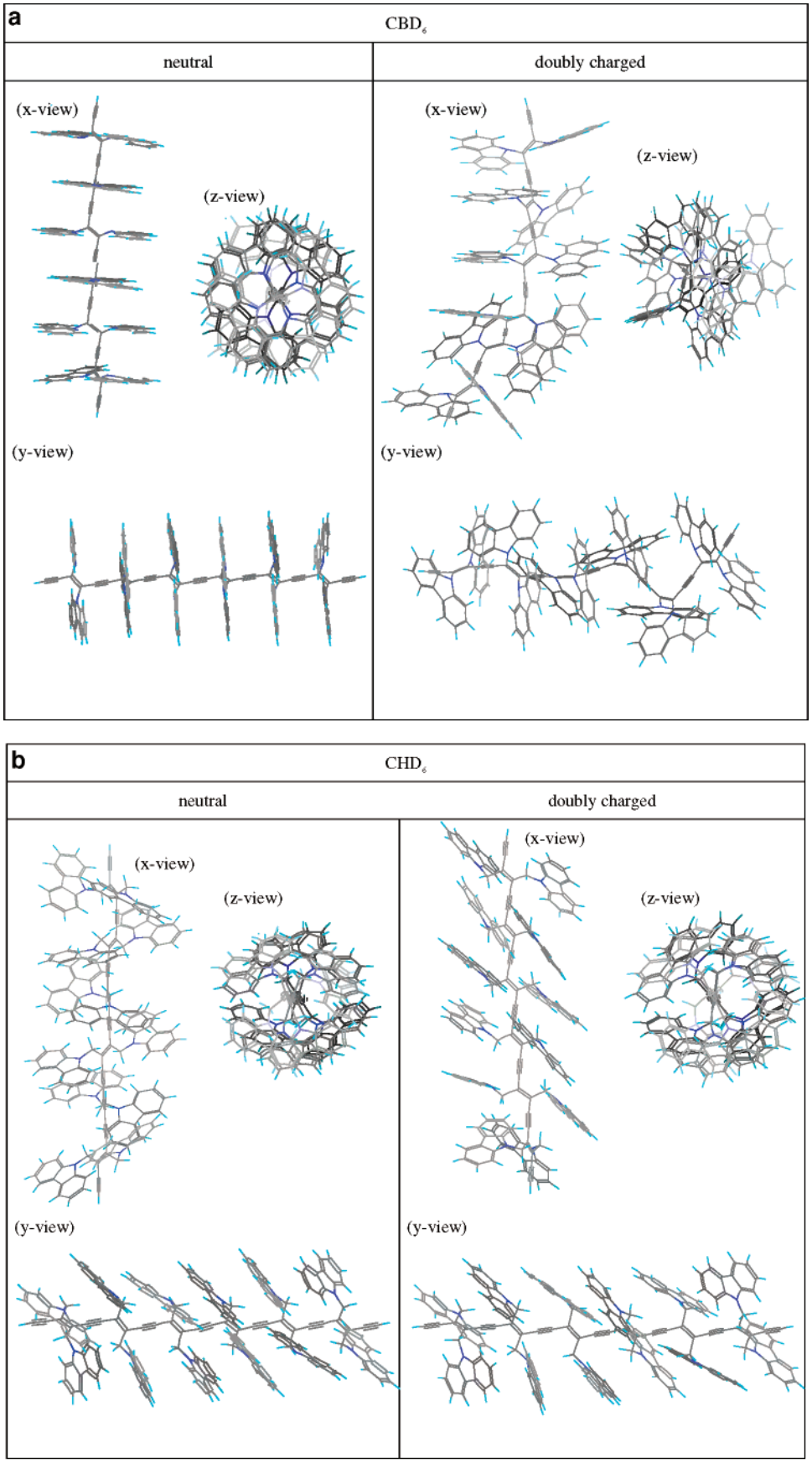


Figure 4. (a) AM1 ground-state optimized geometries for the CBD_6 (a) and CHD_6 (b) oligomers. (b) AM1 ground-state optimized geometries for the CBD_6 (a) and CHD_6 (b) oligomers.

of CEO modes for each case being fixed in advance, the scanned energies window in the absorption spectra results to be reduced as the oligomer size increases. As a consequence for the larger oligomers ($n = 6$ for the neutral and $n \geq 4$ for the charged

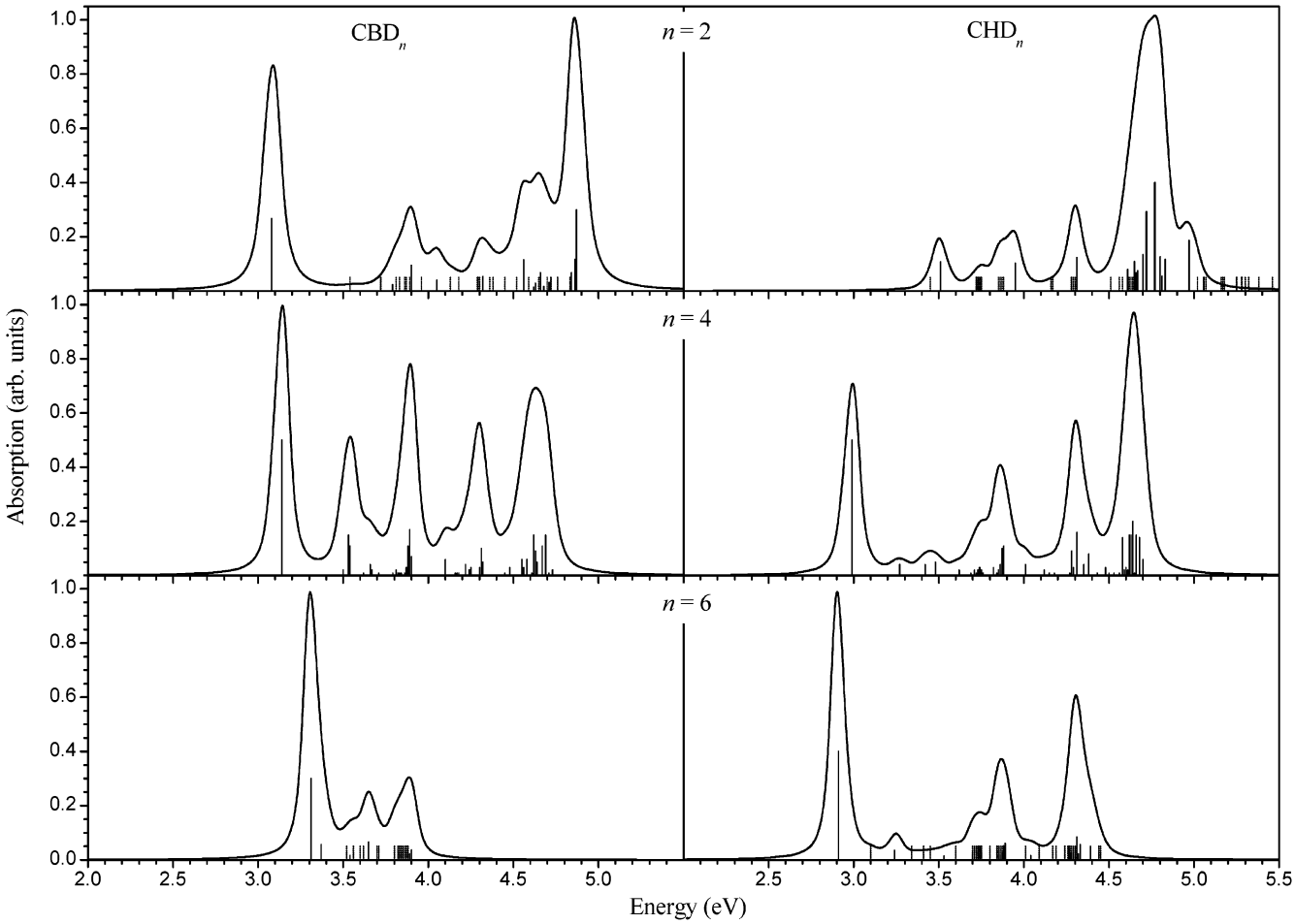


Figure 5. Computed absorption spectra for the neutral CBD_n and CHD_n oligomer. Proportional stick spectra are also reported, where solid (dotted) lines represent allowed (dark) transitions. Each spectrum is normalized to its highest peak.

ones), the higher excitations, which are mostly associated with the carbazolyl moiety, cannot be considered.

In Figure 5, the lowest allowed transition, which will be shown below to be correlated to a backbone excitation, is seen to follow an opposite behavior in the two types of oligomers. The transition blue-shifts with increasing oligomer size in CBD_n (3.08, 3.14, and 3.31 eV for $n = 2$, 4, and 6, respectively) and red-shifts in CHD_n (3.51, 2.99, and 2.91 eV, respectively). Both series (with the exception of CBD_2) are blue-shifted with respect to the corresponding unsubstituted oligomers, which give[28] 3.34, 2.84, and 2.65 eV. This behavior is correlated to the different conjugation lengths in the three types of oligomers. For the unsubstituted oligomer, the total trans geometry allows the most efficient and wide conjugations path,[29] whereas the presence of dihedral angles different from 180° in CBD_n and CHD_n, and the alternative conjugation pathway in CBD_n, reduce the conjugation length of the backbone, as underlined by the plots of the corresponding CEO modes in Figure 6. Only the backbone moieties are displayed in the plots, since for the above transitions small interactions with the carbazolyl substituents occur only in CBD_2 (where their presence explains the lower excitation energy found with respect to the unsubstituted oligomer), whereas they are almost completely absent in the remaining cases. From Figure 6, it is seen that the conjugation length is drastically reduced in CBD_n with respect to CHD_n and to the unsubstituted oligomers[23] (not reported here), due to the fact that the largest deviations from the trans structure occur in CBD_n, as mentioned previously. Specifically, the conjugation length in CBD_n covers about two repeating units, nearly independent of the oligomer size. Most important and despite the geometry distortion, in both systems, interaction between the π electrons of the double and triple bonds is seen to be still possible, due to the presence of two orthogonal π bonds in the latter. This interaction is apparent in the plot relative to CBD_6 in the form of small off-diagonal elements in the region of the C atoms whose label is less than 18. A somewhat different situation, which resembles the unsubstituted case, is found in CHD_n, where the excitation involves the whole backbone, except perhaps the chain ends, and becomes more extended as n increases. In fact, it covers two, about three, and about four repeating units for the dimer, tetramer, and hexamer respectively, which accounts for the computed red-shift.

As a final detail in Figure 5, we finally note that for CBD_n new features appear in the region 3.5÷4.0 eV with respect to the unsubstituted case, which are related to the interaction between the backbone and the carbazolyl moieties. On the contrary, for CHD_n to first order the computed spectra are the superposition of those of the unsubstituted oligomer and of carbazole, as shown in ref 29.

The calculated absorption spectra for the doubly charged case, which can be taken as a model for the photoinduced spectra, are shown in Figure 7 and allow for a few interesting remarks. For the unsubstituted doubly charged systems, the lowest transition energies were calculated at 2.76, 1.95, and 1.54 eV for $n = 2$, 4, and 6 respectively, and only for large n ($\geq$12), the two injected charges could evolve into an ensemble of two interacting polarons, which shows a very low excitation energy (for $n = 15$, 0.25 eV).[28] The corresponding values found for

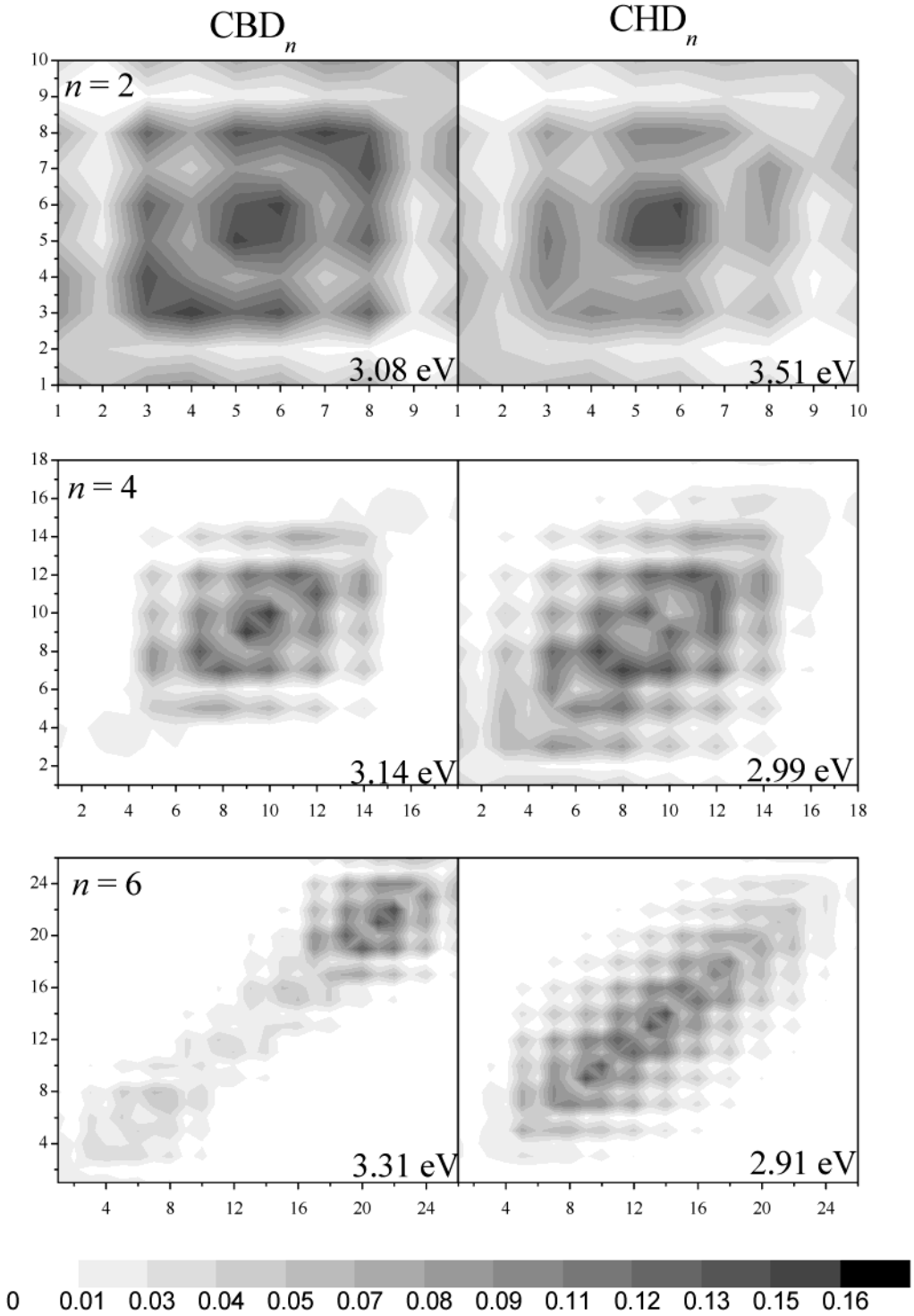


Figure 6. Partial contour plots (see text) of the CEO modes for the lowest optical transitions of the CBD_n and CHD_n neutral oligomers. Bottom: contour scale. The atom labeling is shown in Figure 3.

doubly charged CBD_n (CHD_n) are 1.79 (0.34), 1.67 (0.68), and 0.63 (0.37) eV for $n = 2$, 4, and 6, respectively. The latter transition energies are substantially red-shifted with respect to those of the unsubstituted molecule, and despite the short length of the present oligomers, they are comparable to the result for the large unsubstituted oligomer, especially in CHD_n.

For CHD_6, a peak at 2.3 eV is also present with an appreciable oscillator strength, a transition involving only the backbone which is correlated to the larger amount of trans structure in this oligomer.

Three points in the spectra of Figure 7 deserve a closer examination. First, the lowest excitation energy markedly decreases with increasing n in CBD_n and is almost constant for CHD_n. Second, for CBD_n, the lowest allowed excitation is set well apart from the higher transitions, whereas for CHD_n, a rather large manifold of allowed excitations close in energy is present, which makes the peaks more broadened. Third, the number of dark transitions results to be increased with respect to the neutral oligomers. To get insight on the above points, we report in Figure 8 the full plots of the CEO modes for the transitions referred to above. For CBD_n, the excitation is seen to be localized on the previously discussed butatrienic structure. We remind that such a structure, where an excess charge and a geometry relaxation are strictly connected, is usually called a

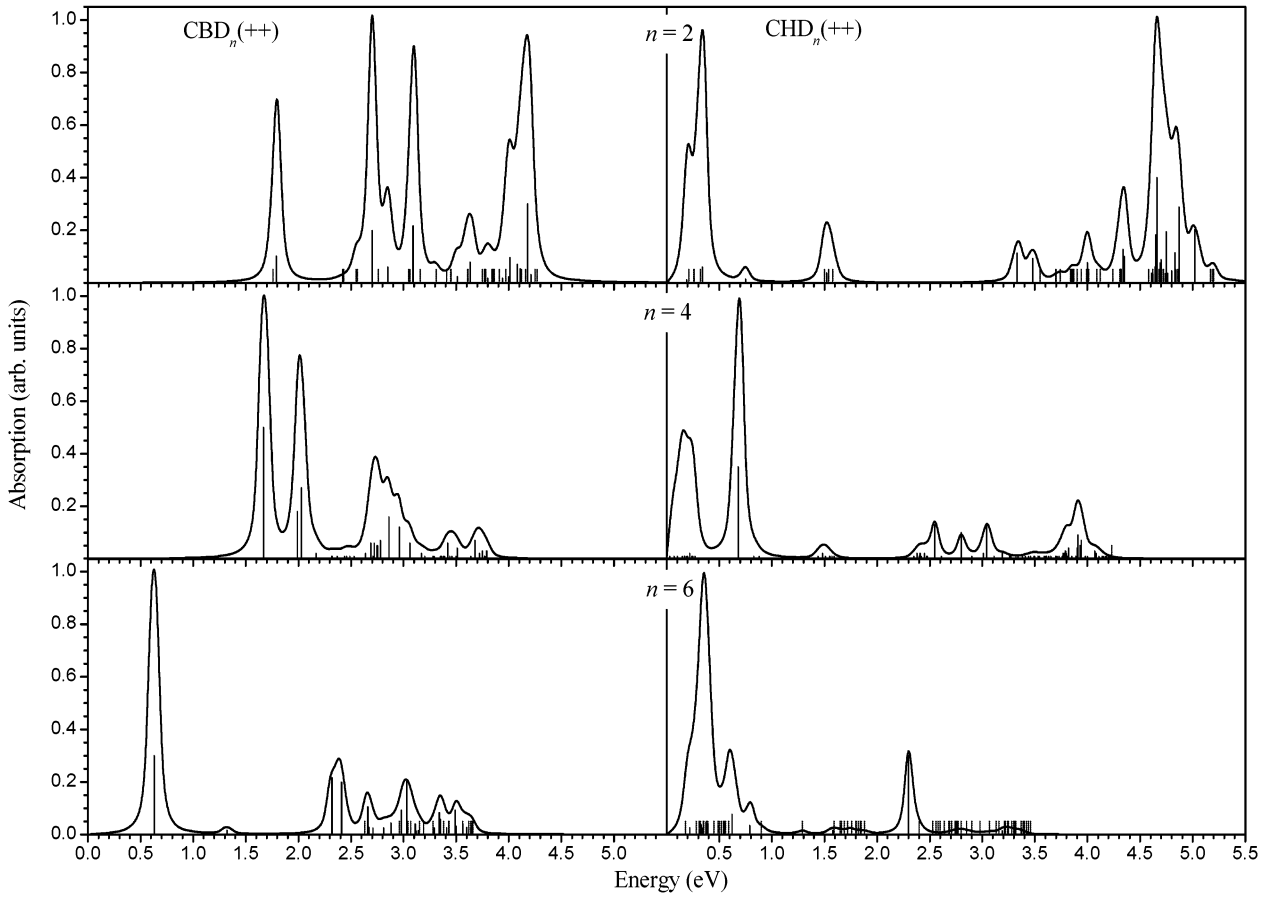


Figure 7. Computed absorption spectra for the doubly charged CBD_n and CHD_n oligomers. Proportional stick spectra are also reported, where solids (dotted) lines represent allowed (dark) transitions. Each spectrum is normalized to its highest peak.

bipolaron or a polaron according to its net global charge. Here interactions between the backbone and the carbazolyl units involved in this structure occur, as shown by the presence of off-diagonal terms in the plots. In the dimer, the excitation has a charge-transfer character (symmetrical off-diagonals elements have different weights), and electrons move from the backbone to the two carbazolyl units in positions II and III, which take part in the bipolaron (see Figure 3), whereas one of the less distorted carbazolyl moieties in position I is concerned with an opposite motion. Similar is the behavior of the tetramer, in which the carbazolyls involved in the bipolaron are in positions IV and V, but the amount of electron transfer toward the latter is somewhat larger, accounting for the slight red-shift of the transition with respect to the dimer. In the inset in the plot, the backbone is shown in detail, and the excitation is seen to be localized on the central section, that is, on the butatrienic structure, as was in the dimer, with small interactions with the remaining bonds. A different situation is found in CBD_6, where the excitation still includes a butatrienic structure but also extends over the rest of the backbone, and charge transfer occurs toward *several* carbazolyl moieties. These features give rise to the large red-shift in this oligomer. To be specific, for the two shorter oligomers, the excitation is dominated by the conjugation path involving one repeating unit and the two adjacent carbazolyls, whereas for the hexamer, such a moiety also interacts with the rest of the molecule, which resembles a neutral tetramer made more nearly planar. This picture clearly emerges from the inset in the plot and is in agreement with the geometry results of section 3.1, as well as with the discussion of the spectra of neutral CBD_n.

Contrary to what one could expect in view of the presence of the CH_2 spacer, it is in the CHD_n series that the largest redshifts with respect to the unsubstituted oligomers are predicted. The energy of the lowest excitation is seen to be practically independent of the oligomer size (the seeming deviation for CHD_4 is due to the different nature of the transition chosen in this case,[23] see also below), the reason for this being that the excitation always involves the whole molecule. This behavior is apparent in the CEO plots and is the counterpart of what previously pointed out in the geometry section. In fact, contrary to CBD_n, for charged CHD_n, there is no bipolaronic structure, but the geometry relaxations are very limited as noted before, the largest effect being the decrease of the backbone dihedral angles toward planarity. In the dimer, the excitation does not carry an appreciable charge transfer character, and there is only a small probability of electron motion from the backbone to the carbazolyls. In the higher oligomers, however, interactions with several carbazolyl moieties occur, and in fact, already for CHD_4 the backbone is completely involved (see inset) in interactions with carbazolyl units in positions IV to VIII. The charge-transfer character of the excitation is apparent, but in this case, *holes* are moving from the backbone to the substituents. The usual behavior is recovered, as could be expected, in the really lowest-energy transition of CHD_4,[29] as well as in CHD_6, where electrons move toward the carbazolyls and in fact the transition energy decreases.

The above results suggest that the latter type of oligomers could be seen, to a first approximation (at least for the excitations below 1.0 eV), as distorted unsubstituted oligomers interacting with a neighborhood of partially charged carbazole molecules. We can recall at this point that the CHD_4 results exhibit a great similarity[29] with the experimental data of the photoinduced absorption spectrum of the corresponding polymer, namely

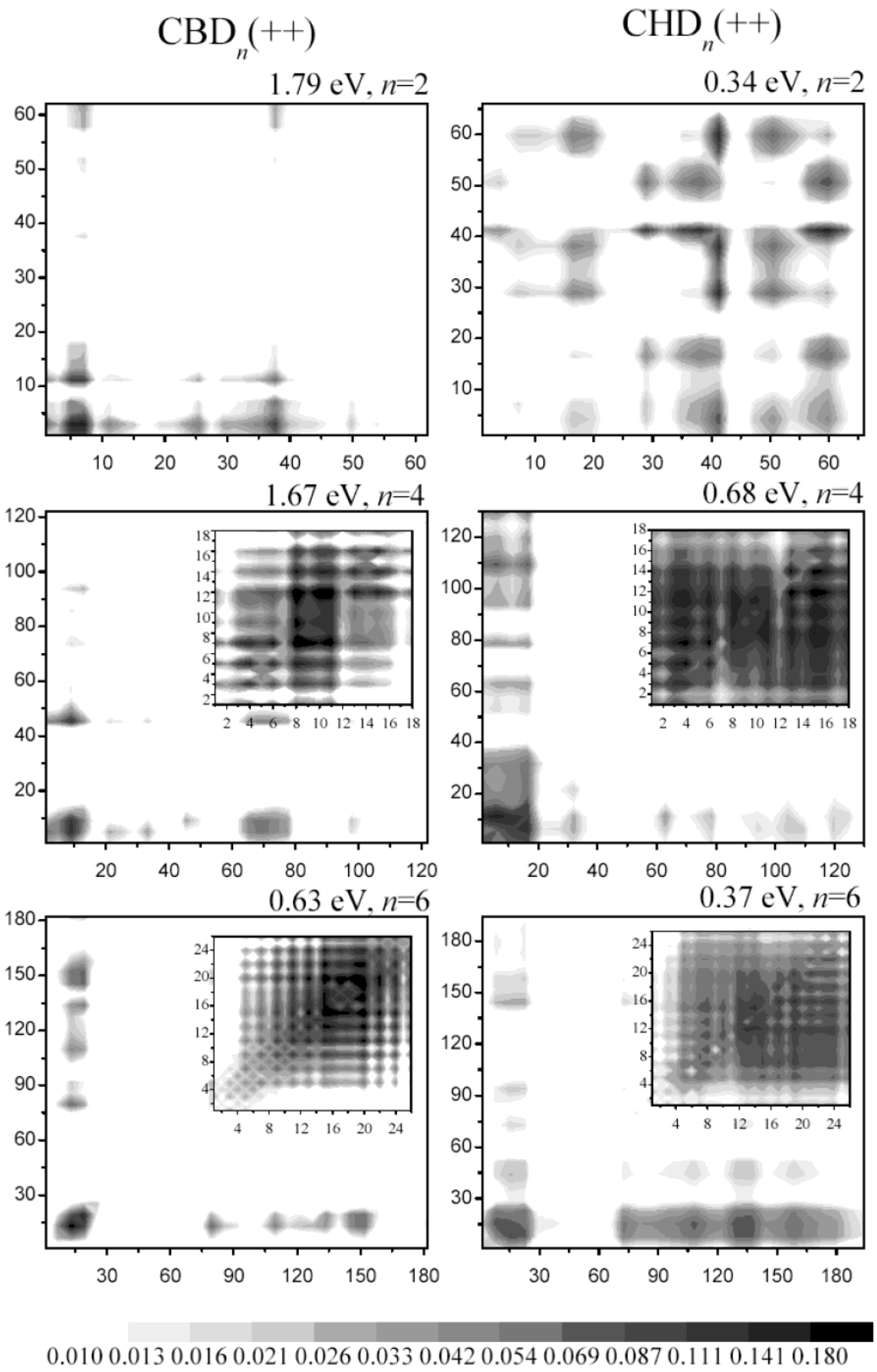


Figure 8. Contour plots of the CEO-modes for the lowest optical transitions of CBD_n and CHD_n doubly charged oligomers. The insets show details of the backbone region. Bottom: logarithmic contour scale. The atom labeling is shown in Figure 3.

polyDCHD[30] which shows two bands at ~0.1 (broadened) and 0.81 eV. The hexamer case is not very different, but the relative oscillator strengths of the manifold of allowed low-energy transitions and of the transition at about 0.68 eV result to be inverted.

4. Conclusion

In the two model systems CBD_n and CHD_n, we have been able to show that substituents effects are not negligible nor easily predictable, especially in the presence of an electronic excitation. In fact, although for CBD_n the chemical structure itself suggests that the carbazolyl moiety can interact with the π electrons of the backbone via the lone pair of the N atom, the possibility of a substituent/backbone interaction in CHD_n is not obvious. In the first case, the π systems of the substituents and of the backbone directly interact, giving rise to an alternative conjugation pathway (or maybe to a more extended conjugation). Such an effect (through-bond interaction[29]) is already present in the neutral oligomer, but it is emphasized when a charge is injected in the structure. On the contrary, in CHD_n or similar oligomers, although the two π systems are not reciprocally conjugated, due to their relative orientation and small distance, an electron flow is seen to take place between them (through-space interaction[29]).

A further remarkable point is the difference in the nature of the excitons associated with the double charge in the unsubstituted, CBD_n and CHD_n oligomers, which in turn can affect the charge transport properties. In the first case, the bipolaronic structure obtained for large oligomers is reminiscent of a system of two interacting polarons.[28] For CBD_n a bipolaronic structure independent of the oligomer size is found, whereas for CHD_n, the excess charge does not give rise to any similarly relaxed structure, but rather to an interaction between the π system of the backbone and the partially charged carbazole moieties.

Finally, CHD_n appears to represent a better model, with respect to our previous investigation,[25] of the nature of the photoexcitons in polyDCHD, in that the predicted low-energy excitations compare more favorably with experimental results.

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