

## ***NLO Response of Clusters of Conjugated Organic Molecules: A Quantum Mechanical Study***

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### **Abstract**

In this work, the effects of the variation of the distances between the monomers of 4-dimethylamino-4'-nitrostilbene molecules constituting various types of clusters on the NLO responses was studied. In these clusters, the fragments can be arranged either parallel, antiparallel or perpendicular with respect to one another. The structure optimization as well as the computation of the NLO parameters were performed using different functionals incorporating different percentages of exchange in combination with 6-31G (d, p) basis set. The studied models are dimers, trimers and quadrimers. A correlation between calculated and experimental NLO parameters allowed us to select the most probable structures.

**Keywords:** *DFT methods; NLO parameters; clusters; hyperpolarisabilities; NBO; Infrared spectra.*

### **Introduction**

Clusters of push-pull molecules have important applications in the fields of photovoltaics<sup>[1]</sup>, non-linear optics<sup>[2]</sup> and nano-catalysis<sup>[3,4]</sup>. In this context, we will give a perception of work carried out on these areas. Ceppatelli *et al.* have shown that the minimum distance between two carbons belonging to a two different diphenylacetylene units arranged in a parallel way in a cluster representing the crystalline state is 3.784 Å<sup>[5]</sup>. In the same order of ideas, when dealing with benzene dimers and with the objective to find out the most favorable arrangement for optimal applications in the field of photovoltaics, Fink *et al.* demonstrated that short distances of around 2.0 to 4.5 Å separating two parallel benzene units in a cluster favor charge (electrons) transfer, while for distances beyond 5 Å, the charge transfer cannot be improved<sup>[6]</sup>. Another work reported by Karami *et al.* on amyloid molecules arranged either as monomer, dimer or trimer, in the two latter cases, the units were also parallel to each other, confirmed using NBO analyses that the intramolecular delocalization increases with

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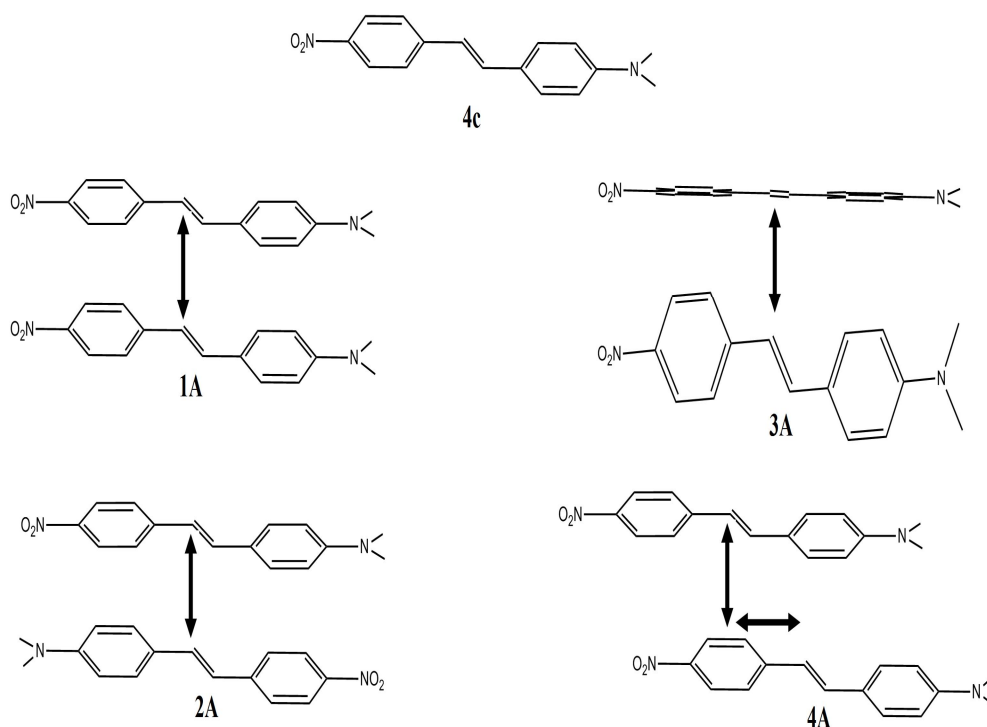
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the number of units<sup>[7]</sup>. On the other hand, the results of theoretical studies carried out on clusters of acetone molecules arranged as cyclic models stacked parallel (for the trimer and the tetramer) were confirmed using Infrared spectroscopy<sup>[8]</sup>. An analog study, both experimental and theoretical, on dimers, trimers and tetramers of toluene stacked either parallel, anti-parallel or perpendicular has concluded that the aggregation starts as two units arranged in a parallel way, while the arrangement becomes random when the number of units increases<sup>[9]</sup>. In the present paper, we consider clusters (dimer, trimer and tetramer) of conjugated organic push-pull molecules. We focus on calculating the NLO parameters, particularly, the first hyperpolarizabilities using the CAM-B3LYP method. We were particularly interested in the role of the arrangement as parallel, anti-parallel or perpendicular as well as the separating distances on the NLO response. The most probable structures were determined using theoretical and experimental hyperpolarizabilities reported in the literature.

### Computational details

All quantum calculations were performed using the Gaussian09 program<sup>[10]</sup>. We first proceeded to a full optimization of the molecule **4c** (*Figure 1*). Then, calculations of structures and energies were carried out using the 6-31g(d,p) basis set combined with hybrid meta DFT methods based on the Kohn–Sham et Hohenberg formalism<sup>[11]</sup> and incorporating in each a given percentage of exchange (XC%). These functionals are the BLYP<sup>[12]</sup>, which is a hybrid functional of the  $\tau$ -dependent gradient-corrected functional of Tao, Perdew, Staroverov and Scuseria TPSSH<sup>[13]</sup>, the most popular functional B3LYP<sup>[14]</sup>, the Perdew–Burke–Ernzerhof PBE0 (pbe1pbe)<sup>[15]</sup>, the Boese and Martin’s  $\tau$ -dependent hybrid functional BMK<sup>[16]</sup>, the M06-2X functional<sup>[17]</sup>, long-range corrected using Coulomb Attenuation Method combined with B3LYP (CAM–B3LYP functional)<sup>[18]</sup> and the Minnesota functional with a full HF exchange M06–HF<sup>[19]</sup>. The corresponding XC percentages are respectively: 0%, 10%, 20%, 25%, 42%, 54%, 20–65% and 100%<sup>[20,21]</sup>. In addition, the long range-corrected version of wPBE, the functional LC–wPBE<sup>[22]</sup>, and second-order Møller–Plesset correlation methods, MP2<sup>[23]</sup>, were also used.

The corresponding first hyperpolarizabilities are reported in Table 1. The weakest deviation compared to experiments was recorded for the MP2 method. While, the second and the third weakest are given by the functionals M062X, CAM–B3LYP and LC–wPBE which gave almost similar deviations. Our choice fell on the functional CAM–B3LYP because it is a long-range functional that gives less computation time compared to the MP2.



**Figure 1:** First series of studied dimers.

**Table 1:** Obtained deviations between calculated and experimental first hyperpolarizabilities ( $\times 10^{-30}$  esu) using different functionals and MP2 methods combined with 6-31G(d,p) basis-set.

Functional	Exchange (%)	$\beta$	MAE (%)
BLYP	0	288.78	246.67
TPSSh	10	236.06	183.39
B3LYP	20	204.38	145.35
PBE0	25	179.71	115.74
BMK	42	152.19	82.70
M062X	54	104.24	25.14
CAM-B3LYP	19 – 65	105.31	26.42
M06HF	100	49.75	40.27
LC-wPBE	0 – 40	61.11	26.63
MP2	–	83.58	0.34
Exp <sup>(1)</sup>	–	83.3	

<sup>(1)</sup> Experimental data derived from References [28,29].

In the gas phase, the CAM-B3LYP method combined with the 6-31G(d,p) basis set was also used to calculate the NLO properties related to clusters constituted of stacked molecules where only single point energies were performed considering different separating distances between the units.

At first, dimer clusters were considered; energies were calculated for separating distances from 3 Å to 10 Å at different orientations as parallel, anti-parallel or perpendicular of one unit with respect to the other one. The structure corresponding to the lower energy was further considered for energy calculations with shifting one unit in one direction. Then, clusters of trimers, tetramers were built from the optimal structure obtained for the dimer. Static hyperpolarizabilities were then calculated and compared with available experimental data.

Since the charge transfer is predominantly responsible of NLO responses in this type of systems, NBO (Natural Bonds Orbitals) analyses were carried out for the considered clusters in the gas phase. The results were interpreted on the basis of delocalization energies  $E(2)$ , energy gaps between LUMO and HOMO orbitals  $\Delta E_{H-L}$  and dipole moments  $\mu_{tot}$ .

Static hyperpolarizabilities  $\beta^{[24,25]}$  and dipole moments<sup>[26]</sup> were calculated according to the following equations:

$$\mu = \sqrt{(\mu_x^2 + \mu_y^2 + \mu_z^2)}$$

$$\beta = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

All these listed components are directly obtained from calculations using Gaussian 09 program.

## Results and Discussion

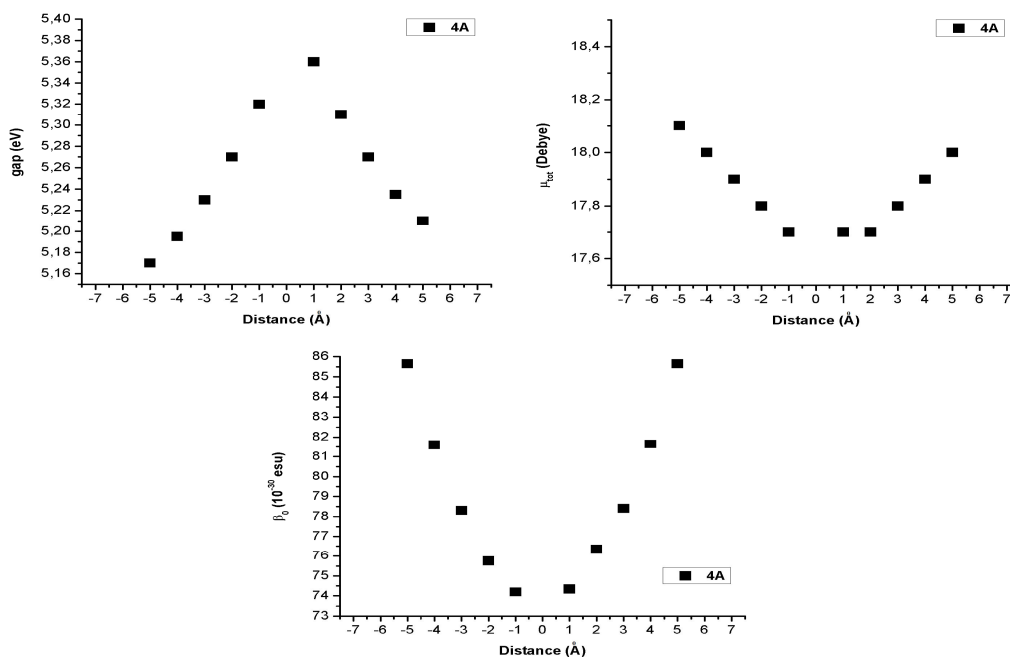
In Table 2, the static first hyperpolarizabilities, the dipole moments as well as the energy gaps are reported for the molecules shown in Figure 1. All these parameters were calculated using the CAM-B3LYP method, which was revealed as very accurate in producing NLO properties<sup>[27]</sup>, in combination with the 6-31G(d,p) basis set.

In this part, three different stackings in dimers were considered: 1A, 2A and 3A in Figure 1. Single point energy was calculated in each case by varying the separating distances between the two units constituting the dimer (this direction is considered as the Z axis) from 3 Å to 10 Å. This range was chosen in accordance with previous reported studies on analog molecules<sup>[6-8]</sup>. The variations of the energy gaps, the dipole moment as well as that of the static first hyperpolarizability with respect to the distances are reported in Table 2 noting that the hyperpolarizability values obtained for the clusters were divided by the number of units in the cluster in order to make objective comparisons with experimental results<sup>[28,29]</sup>. The structure whose properties agree with the experimental results was then selected to assess the effect of shifting

one unit relative to the other from -5 Å to 5 Å in the direction of the molecule axis (considered as X axis) and keeping the optimal distance between the two units constant.

From Table 2, we notice that the energy gaps for systems 1A, 2A and 3A increase with increased intermolecular distance until a distance around 5 Å is reached, after which the variation remains almost constant. This is explained by the presence of a charge transfer between the monomers for distances less than 5 Å, but beyond this value, the charge transfer becomes small or close to zero. On the other hand, the dipole moments increased very slightly when the separating distances increased and this for all systems. However, the static hyperpolarizabilities showed significant increases for the clusters 1A and 3A, but for 2A, we recorded slight decreases.

In the following section, we fixed the separating distance to 5 Å for the system A1 and we shifted one molecule in the direction of its principal axis, the second molecule was kept fixed. For each configuration, the first hyperpolarizability  $\beta_0$  was calculated and compared to the experimental one; the corresponding results are reported in Table 1 and Figure 2. We can note a symmetry on both sides of the value of the shift equal to zero and those which give the closest results to the experimental ones are then, the distances of -4.5 and 4.5 Å.



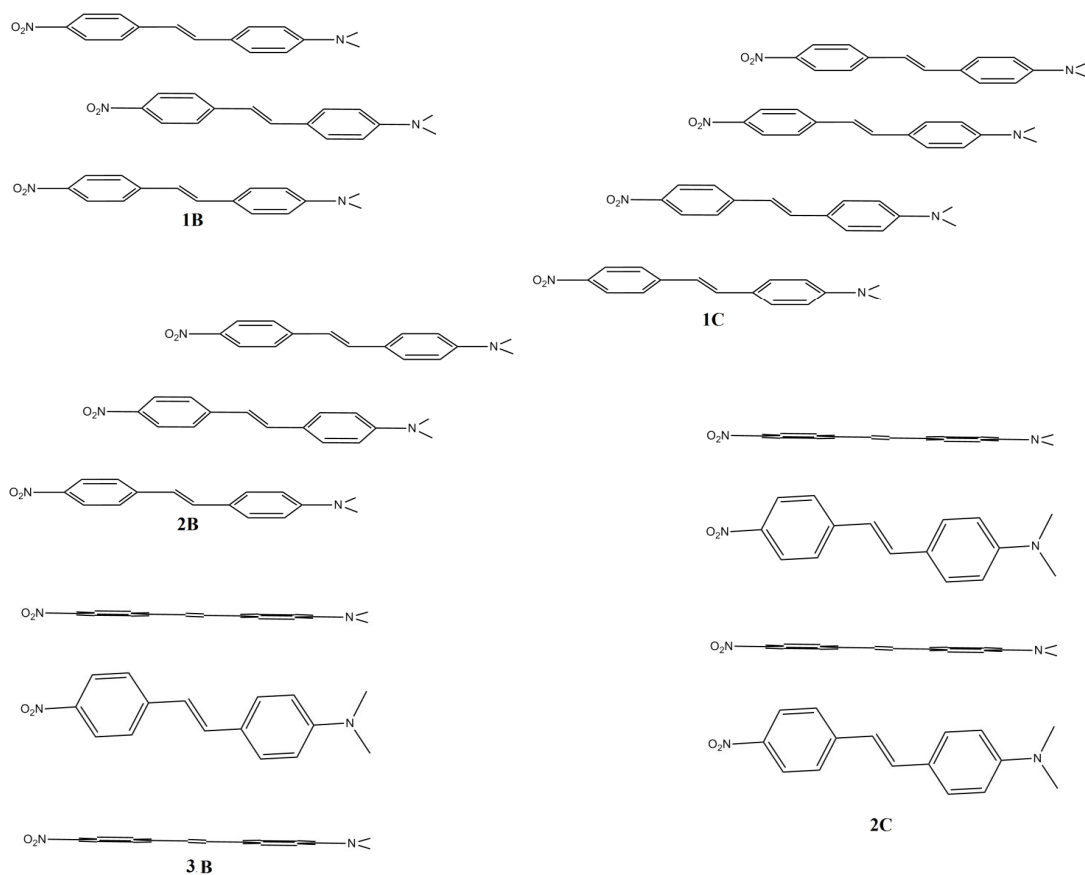
**Figure 2:** Variations of the energy gaps (eV), dipole moments (Debye) and static hyperpolarizabilities with the separating distances between units in the dimer 4A.

**Table 2:** Energy gaps  $\Delta E_{L-H}$  (eV), dipole moments  $\mu$  (Debye), first static hyperpolarizabilities  $\beta_0$  ( $\times 10^{-30}$  esu) calculated using CAM-B3LYP/6-31G(d,p) for the considered dimers.

Translation ( $\text{\AA}$ )		3	3.5	4	4.5	5	6	7	8	9	10
1A	$\Delta E_{L-H}$	4.08	4.79	5.14	5.28	5.36	5.36	5.36	5.36	5.36	5.36
	$\mu_{tot}$	17.1	17.3	17.5	17.6	17.7	17.9	18.0	18.1	18.2	18.3
	$\beta_{tot}$	62.7	64.95	67.9	70.85	73.75	78.95	83.25	86.8	89.75	92.2
2A	$\Delta E_{L-H}$	4.97	5.05	5.09	5.13	5.16	5.19	5.21	5.23	5.24	5.25
	$\mu_{tot}$	0.58	0.53	0.48	0.44	0.41	0.39	0.39	0.38	0.38	0.38
	$\beta_{tot}$	2.5	1.69	1.185	0.845	0.64	0.52	0.37	0.31	0.28	0.265
3A	$\Delta E_{L-H}$	5.19	5.24	5.276	5.29	5.30	5.31	5.32	5.32	5.32	5.32
	$\mu_{tot}$	17.6	17.7	17.8	17.9	17.95	18.1	18.2	18.25	18.3	18.4
	$\beta_{tot}$	72.15	75.15	78.05	80.5	82.7	86.45	89.55	92.05	94.15	95.85
Shift ( $\text{\AA}$ )		-5	-4	-3	-2	-1	1	2	3	4	5
4A	$\Delta E_{L-H}$	5.17	5.195	5.23	5.27	5.32	5.36	5.31	5.27	5.235	5.21
	$\mu_{tot}$	18.1	18.0	17.9	17.8	17.7	17.7	17.7	17.8	17.9	18.0
	$\beta_{tot}$	85.65	81.6	78.3	75.75	74.2	74.35	76.35	78.4	81.65	85.65

From these results, it is concluded that the dimer which reflects best the experimental values is 1A where the two units are parallel to each other and separated by 5 Å and where one unit is shifted by 4.5 Å in the direction defined by the molecule principal axis. This configuration is used to build the trimer and tetramer shown in Figure 3.

In Table 3, the energy gaps for various clusters are reported. It can be seen that the energy gaps are similar for the systems 4C, 3A, 3B and 2C with values much higher than those of the other systems. The second higher values are those of the systems 1A and 2B, the lowest are those related to the systems 2B and 1C for which intramolecular charge transfer (ITC) is expected to play an important role. We observe from Table 2 that the dipole moments values increase double for a dimer compared to the monomer. When dealing with first hyperpolarizabilities calculated for the eight systems by dividing the obtained value by the number of units constituting the cluster and in order to compare with the experimental value available for 4C ( $83 \times 10^{-30}$  esu), it is noted that good agreements are obtained with the systems 1A and 3A while a significant deviation was observed for the monomer and for the systems 2B and 1C (trimer and tetramer) amounting to  $6 \times 10^{-30}$  and  $7 \times 10^{-30}$  esu, respectively.



**Figure 3:** Second series of studied systems

**Table 3:** Energy gaps  $\Delta E_{L-H}$  (eV), dipole moments  $\mu$  (Debye), first static hyperpolarizabilities  $\beta_0$  ( $\times 10^{-30}$  esu) calculated using CAM-B3LYP/6-31G(d,p) for the considered monomer, dimers, trimers and tetramers.

	Molecules/ Clusters	$\Delta E_{L-H}$	$\mu$	$\beta_0$
Monomer	4C	5.30	9.36	105.3
Dimers	1A	5.22	17.97	83.5
	3A	5.30	17.95	82.7
Trimers	1B	5.20	26.30	72.1
	2B	5.12	26.50	76.8
	3B	5.29	26.48	74.9
Quadrimers	1C	5.04	35.06	77.0
	2C	5.31	34.86	70.0

From these observations, it can be deduced that the most probable structures for ONL applications are: a) the parallel dimer 1A with a separating distance of 5 Å along the Z axis and 4.5 Å along the X axis, b) the perpendicular dimer 3A with a separating distance of 5 Å along the Z axis, c) the parallel trimer 2B with a separating distance of 5 Å along the Z axis and 4.5 Å along the X axis and d) the parallel quadrimeter 1 C with a separating distance of 5 Å along the Z axis and 4.5 Å along the X axis.

In the experimental work measuring the NLO parameters, the samples are presented as films positioned parallel to each other between slides, all directed towards the incident beam<sup>[28,29]</sup>. This is in the sense of the results achieved in this work.

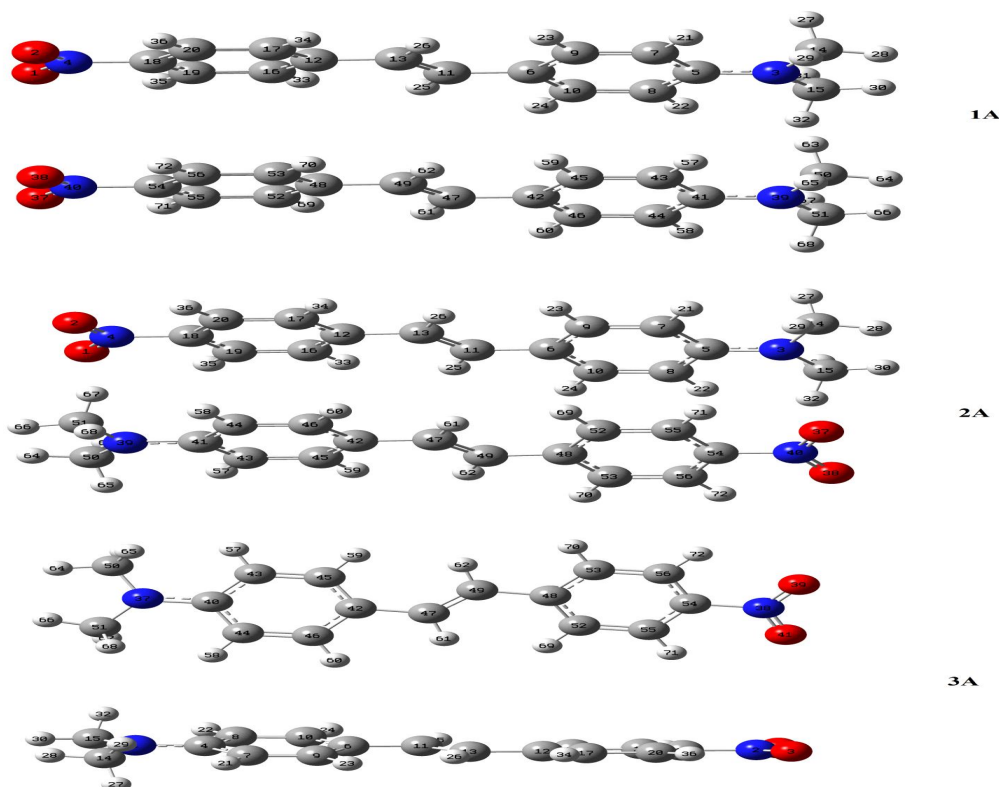
### Natural Bond Orbitals (NBO) analysis

Results from NBO analysis are reported in Table 4. The delocalization energy  $E(2)$  (or stabilization energy) from one monomer towards the other one helps to identify the pathway of the charge transfer in the three systems 1A, 2A and 3A.  $E(2)$  is expressed as a second order perturbation as given in [30-32], where  $q_i$  is the occupation of the donor orbitals,  $\epsilon_i$  et  $\epsilon_j$  are the diagonal elements (orbital energies) and  $F(i,j)$  are the diagonal-off elements of the Fock matrix<sup>[33,34]</sup>. The calculations were carried out using the CAM-B3LYP/6-31G(d,p) level of theory. Atomic numbering is that shown in Figure 4.

The results listed in Table 4 reveal a decrease of delocalization energy  $E(2)$  from the first unit towards the second. This is followed by a total absence of interactions reflected in zero values of  $E(2)$  beyond 5Å for the three systems. At the same time, the hyperpolarizabilities decrease when the distances decrease. It is to note that the interactions are perceptible on the donor and acceptor groups and not on



the chromophores. The NBO analysis was done for distances equal to 5Å for the five remaining systems and therefore, interactions were completely absent in those cases.



**Figure 4:** Atomic numbering in dimers 1A, 2A, 3A.

**Table 4:** Central bond lengths  $R_{C-C}$  (Å), Energy gaps  $\Delta E_{L-H}$  (eV), occupations  $\pi^*/\pi$  and stabilization energies  $E(2)$  (kcal.mol<sup>-1</sup>) calculated by CAM-B3-LYP /6-31G(d,p).

Translation (Å)		3	3.5	4	4.5	5	6	7	8	9	10
1A	$\sigma$ (C14-H29) $\sigma^*$ (C50-H63)	15.3	2.65	0.50	0.09	0	0	0	0	0	0
	$\sigma$ (C15-H32) $\sigma^*$ (C51-H67)	13.3	2.6	0.54	0.11	0	0	0	0	0	0
2A	$\pi^*$ (C18-C20) $\pi^*$ (C41-C44)	29.2	4.19	0.68	0.09	0	0	0	0	0	0
	$\pi^*$ (C16-C19) $\pi^*$ (C43-C45)	5.09	4.24	0.70	0.10	0	0	0	0	0	0
3A	$\pi$ (C6-C10) $\pi^*$ (C46-C60)	0.09	0.06	0	0	0	0	0	0	0	0

## Conclusions

This work deals with the calculations of the first static hyperpolarizability  $\beta_0$  for a single push-pull molecule arranged in various clustering forms (monomer, dimer, trimer and quadrimer in several orientations (parallel, antiparallel and perpendicular). Energies as well as NLO parameters were calculated using the CAM-B3LYP/6-31G(d,p) level of theory. The main goal was to assess the impact of the variation of the separating distances between the units (shifts according to Z axis and shifts according to the principal axis of each unit, the X-axis). This study showed that the most optimal structures for ONL applications are the parallel dimer 1A with a distance 5 Å along the Z axis and 4.5 Å along the X axis, the perpendicular dimer 3A with a distance 5 Å

along the Z axis, the parallel trimer 2B with a distance 5 Å along the Z axis and 4.5 Å along the X axis and the parallel quadrimer 1C with a distance 5 Å along the Z axis and 4.5 Å according to the X axis. NBO analyses through the calculated delocalization energie E(2) confirmed that the separating distances between the units constituting the clusters, is equal to 5Å. At such a configuration, the calculated hyperpolarizabilities are very close to the experimental ones.

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