

Quantum mechanics study on the nonlinear optical responses of a series of 4-hydroxy, 4'-cyanoazobenzene dimers

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Abstract. Nonlinear optical (NLO) properties are mainly measured by the first hyperpolarizability $\beta(0)$ magnitudes. Besides analyzing the NLO behaviours of monomers, dimerization of chromophores has been found of a huge interest for the application in several optical areas. In the present work, a theoretical study has been carried out on a series of dimers constituted by the azo-chromophore 4-hydroxy, 4'-cyanoazobenzene (HCAB). Combinations of vinylic and styrenic oligomers as well as of 1,3-diphenyl propane (1,3-DPP) to HCAB have been also investigated. No influence of geometrical parameters has been detected. Indeed, after establishing a comparison with $\beta(0)$ of monomeric entities, results show that the NLO response of these dimers is not guided by any additivity rule.

1. Introduction

Nonlinear optical (NLO) devices are of a huge interest in the technology of photonics and optoelectronics as well as in several telecommunication applications [1-3]. For any system, the capacity of responding to the nonlinear optical standard is, mainly, measured by the first hyperpolarizability magnitude [4-5]. For this aim, the system should be noncentrosymmetric, and a charge transfer should take place from an electron donor to an electron acceptor through a π -spacer. Organic chromophore systems represent potent candidates in nonlinear optics. Besides their monomers, it would be interesting to analyze dimers and trimers of these chromophores, mainly, to elucidate their NLO behavior.

In the present work, several ways of dimerization of the azo-chromophore 4-hydroxy, 4'-cyanoazobenzene (HCAB) are reported. Static first hyperpolarizability $\beta(0)$ calculations have been carried out, by means of quantum mechanics (QM) and a comparison has been established between the monomer and the different modeled dimers.

Generally, to prepare photoconductor films, chromophores are dissolved in thermoplastic amorphous matrix. This latter contains NLO-phores either as dispersed guest molecules or covalently attached to the polymeric systems. We reported, previously, a case of chromophores covalently grafted on methacrylate copolymers [6]. However, we present here, dimerization of the chromophore model with vinylic and styrenic oligomers, and with 1,3-diphenyl propane (1,3-DPP) which represents a

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covalent combination of two styrene molecules, in order to simulate the dispersion of the chromophore in the polymeric matrix.

2. Static first hyperpolarizability β

When a strong electric field E is applied on a molecule, there is no linearity between the dipoles and the incident field. The polarization P is expressed as a Taylor series expansion as following

$$P = P_0 + \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots \quad (1)$$

where χ_n is the n order susceptibility

At the microscopic level, the polarization can be expressed as

$$P_i = \sum_j \alpha_{ij} E_j + \frac{1}{2} \sum_{j,k} \beta_{ijk} E_j E_k + \frac{1}{6} \sum_{j,k,l} \gamma_{ijkl} E_j E_k E_l + \dots \quad (2)$$

where α_{ij} is the linear polarization, β_{ijk} and γ_{ijkl} are first and second hyperpolarizabilities, respectively.

With regard to dipole moment, equation (2) can be expressed as

$$\mu(E_i) = \mu_i^0 + \sum_j \alpha_{ij} E_j + \frac{1}{2} \sum_{j,k} \beta_{ijk} E_j E_k + \frac{1}{6} \sum_{j,k,l} \gamma_{ijkl} E_j E_k E_l + \dots \quad (3)$$

where μ_i^0 is the dipole moment in the absence of the electric field. Consequently:

$$\alpha_{ij} = \left. \frac{\partial \mu_i}{\partial E_j} \right|_{E=0} \quad (4)$$

$$\beta_{ijk} = \left. \frac{\partial^2 \mu_i}{\partial E_j \partial E_k} \right|_{E=0} \quad (5)$$

$$\gamma_{ijkl} = \left. \frac{\partial^3 \mu_i}{\partial E_j \partial E_k \partial E_l} \right|_{E=0} \quad (6)$$

In centrosymmetric systems, β_{ijk} term vanishes. This tensor is the third derivative of energy:

$$\beta_{ijk} = - \left. \frac{\partial^3 U}{\partial E_i \partial E_j \partial E_k} \right|_{E=0} \quad (7)$$

3. Results

Calculations have been carried out with Gaussian03 program package [7]. A Full optimization in gas phase has been performed at B3LYP/6-31+G(d,p) level of theory, on several dimers of 4-hydroxy, 4'-cyanoazobenzene (Figure 1). Subsequently, their static first hyperpolarizabilities have been calculated at HF/6-311+G(d) level.

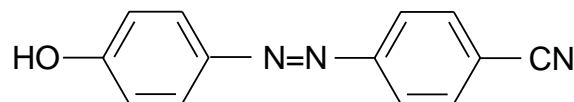


Figure 1. Structure of 4-hydroxy, 4'-cyanoazobenzene (HCAB).

With the Kleinman symmetry [8] contribution, total static first hyperpolarizability $\beta(0)$ is calculated by the combination of nine tensor elements provided by the program as

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (8)$$

Dipole moments μ and first static hyperpolarizabilities $\beta(0)$ magnitudes of the different HCAB dimers and of dimers constituted by HCAB combined to styrene, to 1,3-DPP and to a vinylic octamer, respectively, before and after optimizations are regrouped in Table 1. Dimers geometries have been built by positioning the two molecules one parallel to the other (Par), in the same plane (Plan), and one perpendicular to the other (Per), respectively.

Table 1. Dipole moment (μ , D), initial and final static first hyperpolarizabilities ($\beta(0)$, X 10^{-30} esu) and HOMO-LUMO energy gap (ΔE_{H-L} , a.u.) of the different dimers studied.

	μ	$\beta_{initial}(0)$	$\beta_{final}(0)$	ΔE_{H-L}
HCAB-HCAB-Par	13.27	25.59	34.48	0.126
HCAB-HCAB-plan	12.84	33.42	34.16	0.126
HCAB-HCAB-Per	11.18	37.79	41.65	0.103
HCAB-Styrene	6.95	21.41	21.37	0.121
HCAB-1,3-DPP	6.83	11.41	18.59	0.130
HCAB-Oct-Par	6.63	17.18	23.33	0.096
HCAB-Oct-Per	8.08	16.13	25.11	0.071
HCAB	6.87		41.60	
Styrene	0.21		0.54	
1,3-DPP	0.44		0.61	
Octamer	0.0014		0.0078	

The final geometries of the studied dimers reveal a perpendicular shape. An enhancement of the $\beta(0)$ magnitudes is noticed from the initial to the final geometries, especially, for the HCAB dimer positioned in the plane. The highest $\beta(0)$ value is attributed to the T-shape of HCAB dimer (perpendicular), probably due to the electronic delocalization enhanced by the azo group and the lone pair of nitrogen atom which accentuates the OH donor effect.

Despite the fact of the existence of two styrene molecules in the HCAB-1,3-DPP dimer, its $\beta(0)$ magnitude is smaller than that one containing only one styrene. This is probably due to the existence of a simple bond in 1,3-DPP which reduces the electronic delocalization effect.

The comparison between $\beta(0)$ of the HCAB monomer and those of its three different dimers indicates that dimerization does not bring any amelioration with regard to the NLO response. Indeed, this fact occurs regardless to the position of the dimers entities.

When HCAB is dimerized by an octamer, $\beta(0)$ magnitudes decrease by about 41% for both parallel and perpendicular geometries. It decreases by 48 % for styrene and up to 55% for 1,3-DPP. This shows that the addition of molecules, even with a significant electronic delocalization, to HCAB chromophore does not contribute to the enhancement of $\beta(0)$.

On the other hand, it is shown from Table 1 that although $\beta(0)$ of octamer is smaller than those of styrene and 1,3-DPP, its dimer with HCAB possesses the largest $\beta(0)$ value.

Seemingly, $\beta(0)$ values are decreased by a factor of about 1.2 when HCAB is dimerized with another HCAB and with a factor of 2 once it is dimerized with octamer or styrene.

The energy gap between the frontier orbitals, high occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been analyzed in Table 1. In the series of HCAB-

HCAB dimers, it is shown that the dimer in the perpendicular geometry seems to be the most excitable molecule due to its lowest ΔE_{H-L} . Concomitantly, the highest energy gap is recorded for HCAB-1,3-DPP dimer. So far, these conclusions are in good agreement with the behavior of $\beta(0)$, where the lower is ΔE_{H-L} , the larger should be $\beta(0)$. However, some exceptions in this classification are noticed concerning dimers containing octamer. In fact, their energy gaps are smaller than that one of HCAB-HCAB-per but their $\beta(0)$ are still smaller than the latter system. It should be mentioned that in the case of HCAB-Oct dimers and unlike all the rest of the other dimers, LUMO are concerned by the octamer rather by HCAB molecule. This can be the reason for the weak character of ΔE_{H-L} for dimers holding the octamer.

4. Conclusion

In the present work, we reported the NLO behavior of a series of dimers composed of HCAB chromophore. It has been noticed that $\beta(0)$ of these dimers are not affected by the geometrical position of the constituents within the dimer. Compared to the NLO response of HCAB monomer, no valuable amelioration has been detected after dimerization.

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