

Polarizabilities of Push-Pull Carbon Nanotubes: Semi-Empirical PM6 Study

Nouar Sofiane LABIDI, Zineb KABIER

Abstract- A series of push-pull armchair (5,5) single-walled carbon nanotubes (D-CNTs-NO₂) saturated with hydrogen at the ends have been studied using semi-empirical PM6 methods. As a result, it is found that the polarizability strongly depends on the strength of Π -electron donor substituent. Particularly, for both static and dynamic polarizabilities the largest increment of $\Delta\alpha$ is seen to be due to -NMe₂ donor group ($\Delta\alpha=100$ a.u.). Miller QSAR-polarizability, empirical models based on molecular volumes (V_m) and electrons number (Ne) correlate well ($R>0.97$) with PM6 polarizabilities results.

Index Terms— PM6, Carbon Nanotube, Polarizability, Push-Pull.

I. INTRODUCTION

In recent years, a lot of research effort has been devoted to second-order nonlinear optical of carbon materials such as carbon black and fiber [1,2] fullerenes [3] carbon nanotubes (CNTs) [4] and graphene [5] due to their potential applications in electro-optics, aerospace and biotechnology fields [2,6-8]. Carbon nanotubes (CNTs) with large delocalized π -electron systems may exhibit extremely larger nonlinear responses, fast electronic response, and low dielectric constant at optical and radio frequencies [9,10]. Great interest has been devoted to predicting linear and nonlinear optical (NLO) response properties of these systems [11,12]. In particular, the prediction of static and dynamic polarizabilities have been received much attention [13-16]. Nanotube polarizabilities are critical for understanding their physical properties and provide us novel insights into their applications as electro-optical devices [17-19]. For the development of these applications, progress in designing new compounds are still expected. Theoretical treatment of the physicochemical properties of carbon tubes in terms of diverse approaches semiempirical [9], ab initio [16], and DFT [20], is, therefore, an important issue.

In this study, we connect in the molecular polarizabilities responses in a series of interesting push-pull (D-CNTs-NO₂) single walled armchair carbon nanotube (5, 5) candidates (Figure 1). To the best of our knowledge, no studies on static and dynamic polarizabilities of modified forms finite

push-pull carbon nanotube (CNTs) have been carried out using semi-empirical PM6 methods. Hence in this work we have calculated mean static and dynamic polarizabilities and polarizabilities tensor components for substituted tubes (D-CNTs-NO₂) at the PM6 levels together with QSAR-quality empirical polarizability using Miller's scheme and molecular volume calculations.

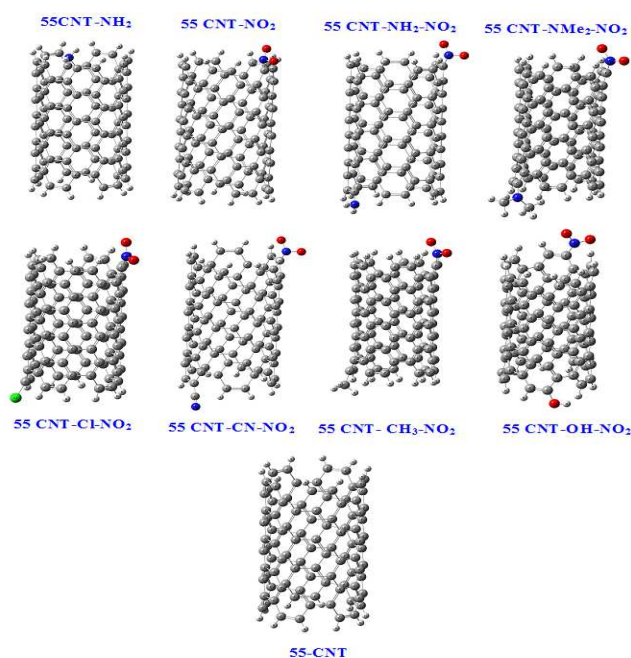


Figure 1: Optimized structure of push-pull (NO₂-CNT-D) armchair nanotubes (5.5).

II. COMPUTATIONAL DETAILS

The geometry of push-pull (D-CNTs-A) single walled armchair carbon nanotube (5,5) with saturated hydrogen atoms at tube ends. Were fully optimized through the MM+ force field using HyperChem v8 [21]. Static and dynamic polarizabilities were evaluated by the semi-empirical quantum chemical method Parametric Method (PM6) [22]. The TDHF calculations were carried out using the common wavelengths ($\omega=0$ and $\omega=1064$ nm). Molecular volumes and Miller-Savchik polarizabilities were calculated from optimised MM⁺ geometries [21].

Nouar Sofiane LABIDI, Department of Materials Sciences, Institute of Science and Technologies. University Centre of Tamanrasset, BP (10034) Sersouf-(11000)-Algeria. LABIDI19722004@YAHOO.FR

Zineb KABIER, Department of Materials Sciences, Institute of Science and Technologies. University Centre of Tamanrasset, BP (10034) Sersouf-(11000)-Algeria. Zinab.kabier@gmail.com
Tel/Fax: (213-29)34.91.86

III. RESULTS AND DISCUSSION

III.1. EFFECTS OF ELECTRON ACCEPTOR/DONOR SUBSTITUENTS ON POLARIZABILITIES.

In order to study the influence of donor /acceptor substitutions on the polarizability, we achieved substitution of two stronger donors (acceptor) groups isolated or in the joint form on the terminal carbon atom of carbon nanotube (CNTs).

The results of static and dynamic polarizabilities (α) using semi-empirical PM6 method for substituted carbon nanotube (Figure.1) are given in Table 1.

Table 1: Static and dynamic polarizability. (The α values are given in atomic units (1.0 a.u. polarisabilité = $1.6488 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1} = 0.14818 \text{ \AA}^3$).

D-CNTs-NO ₂ (5,5)	$\omega=0$	$\omega=1239 \text{ nm}$
	$\langle \alpha \rangle$ (a.u)	$\langle \alpha \rangle$ (a.u)
H-CNTs-H	1133.86	1176.22
H-CNTs-NH ₂	1155.97	1203.79
H-CNTs-NO ₂	1164.69	1219.86
OH -CNTs-NO ₂	1177.70	1227.53
CH ₃ -CNTs-NO ₂	1183.01	1235.52
Cl-CNTs- NO ₂	1187.97	1241.67
NH ₂ -CNTs-NO ₂	1188.03	1240.25
CN-CNTs-NO ₂	1191.19	1284.03
NMe ₂ -CNTs-NO ₂	1221.40	1276.42

Table 1 compares the calculated values of static and dynamic polarizabilities for push-pull (D-CNTs-A) armchair single-walled carbon nanotube with PM6 method. For all tubes the dynamic polarizabilities are slightly higher than the static one's the percent difference is about 4-7%. From compounds under study, the smallest and the largest enhancement of average polarizability are due to the pairs -NO₂/-OH and -NMe₂/-NO₂ respectively. For both static and dynamic polarizabilities the largest increment of $\Delta\alpha$ is seen to be due to - NMe₂ donor group $\Delta\alpha = 88$ (a.u.) and the two smallest increments are due to -OH and -CH₃ donor groups respectively $\Delta\alpha=44$ and 49 (a.u.). Substituted groups methyl (-CH₃), hydroxyl (-OH) and halogen (-Cl) produce modest enhancements of the first hyperpolarizability. Perhaps surprisingly, dialkylamino(-NMe₂) substitution produces a greater enhancement of mean polarizability and also leads to an increase of longitudinal polarizability α_{xx} . Carbon tubes with dialkylamino (-NMe₂) group show 8% and 6% increase of static and dynamic polarizabilities with comparing to a molecule with (H,H) and (H,NH₂) donor groups, respectively.

Our results, performed with semi-empirical PM6 method, reveal that for all push-pull (D-CNTs-A) armchair single-walled carbon nanotube when hydrogen atoms were substituted by, and -NO₂ which is especially strong electron Acceptor, their linear polarizabilities became larger to a certain extent than that unsubstituted (H-CNTs-H) tubes. The results indicate also that the magnitude of polarizability of carbon nano tubes is dependent upon the availability of the

lone pair of electrons on the nitrogen atom to conjugate with the tubular tubes.

As regards to the π -electron donating capacity of the typically substituted groups, we are able to propose a decreasing classification, relatively to polarizability. The established order is as follows: NO₂-CNTs-NMe₂ > NO₂-CNTs-CN > NO₂-CNTs-NH₂ > NO₂-CNTs-Cl > NO₂-CNTs-CH₃ > NO₂-CNTs-OH > NO₂-CNTs-H > NH₂-CNTs-H > H-CNTs-H.

To appreciate the evolution of static polarizability as a function of molecular volume with varying substitution patterns, we calculated the relative efficiency parameter polarizability density: ($\rho = \langle \alpha \rangle / V$) where V is the molecular volume [21]. It can be seen from Figure. 2 that polarizability density depends more on the nature of the donor groups, small substituted groups -CH₃, -Cl and -OH powerfully reduces ρ values. For the strong substituent with (-N) heteroatom (-NH₂ and -CN) the polarizability density varies almost in the same order of molecular volume, they produce the larger polarizability density as compared to the smallest ones.

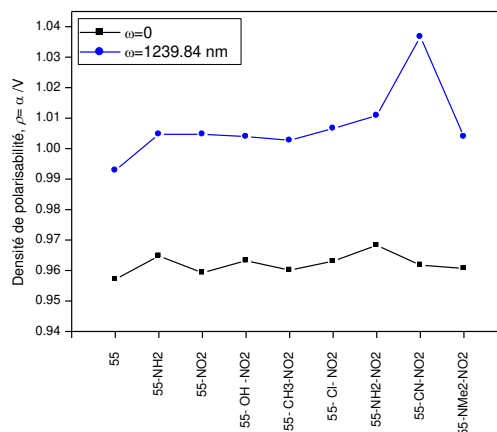


Figure 2: Dependence of the polarizability density for substituted tubes.

III.2. QSAR-QUALITY CALCULATIONS

Polarizabilities are often used in quantitative structure-activity relationship (QSAR) studies, where the aim is to give a reliable but quick estimate of $\langle \alpha \rangle$. We consider the likely reliability of various easily computed indices such as the molecular volume, the Miller empirical volume polarizabilities and PM6 polarizabilities discussed above. The reference in this field appears to be that due to Miller and Savchik [23] with their proposed functional form of polarizability: as in (1).

$$\langle \alpha \rangle = 4\pi\epsilon_0 \frac{4}{N} \left(\sum_A \tau_A \right)^2 \dots \dots \dots (1)$$

where τ_A is an atomic hybrid component for each atom A in a given state of hybridization and N is the total number of electrons. The most computer packages quote the results as polarizability volumes (typically \AA^3). These are shown in Table 2.

Table 2: Molecular volume and Miller polarizability for Y-CNTs-NO₂.

Nanotube (5,5)	$\langle\alpha\rangle$ au	Volume / Å ³	$\langle\alpha\rangle$ Miller / Å ³
H-CNTs-H	1133.93	2019.98	142.94
CNTs -NH ₂	1155.97	2044.83	144.29
CNTs -NO ₂	1164.69	2096.85	145.56
OH -CNTs-NO ₂	1177.70	2112.38	146.20
CH ₃ -CNTs-NO ₂	1183.01	2141.08	147.40
Cl-CNTs-NO ₂	1187.97	2134.89	147.49
NH ₂ -CNTs-NO ₂	1188.03	2122.23	146.92
CN-CNTs-NO ₂	1191.19	2718.83	155.10
NMe ₂ -CNTs-NO ₂	1221.40	2211.35	150.49

For push-pull (D-CNTs-A) single-walled carbon nanotube the Miller method gives a mean polarizability in much better agreement with the semi-empirical PM6 value than the molecular volume. Linear regressions were done for each of these quantities against the semi-empirical PM6 mean polarizabilities $\langle\alpha\rangle$ and the correlation coefficients R are given (Figure 3a and 3b).

$$\alpha^{PM6} = 624.22478 + 1.30435.V_{CNTs} (R=0.96946)$$

$$\alpha^{PM6} = 27.56239 + 0.10186.\langle\alpha\rangle_{Miller} (R=0.99496)$$

The two correlation coefficients are well above 0.97, which value if often taken to justify a straight line relationship. It, therefore, seems that the PM6 simpler procedures give a reliable estimate of $\langle\alpha\rangle$ for these series of molecules.

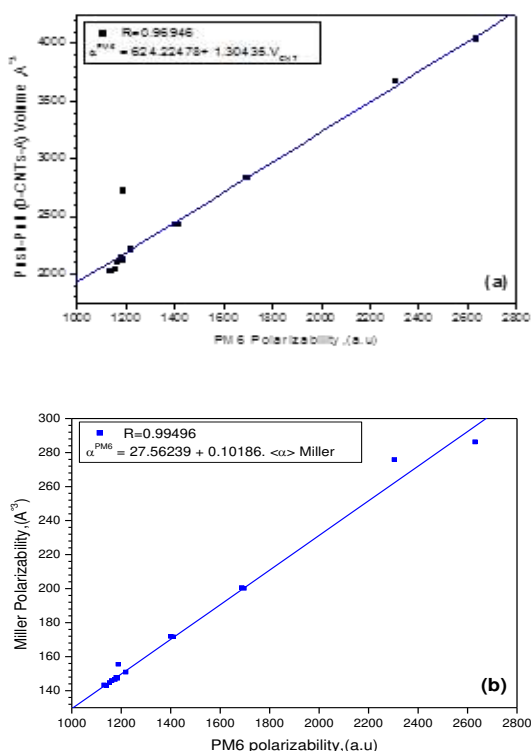


Figure 3: PM6 polarizability of substituted CNTs versus calculated: (a) Molecular volume and (b) Miller polarizability.

The graphical representations of static and dynamic mean polarizabilities versus the number of electrons are shown in Figure.4. It is apparent from this figure that there are

significant correlations among mean polarizabilities and the number of electrons. Both polarizabilities have a linear relation with N_e . The linear regression equations are:

$$\omega=0 : \langle\alpha\rangle = 136.54634 + 4.74919.N_e (R=0.97445)$$

$$\omega=1239 \text{ nm} : \langle\alpha\rangle = -68.31792 + 5.93726.N_e (R= 0.9035)$$

The excellent quality of linear correlation is evident from R coefficients, which are shown above 0.97, Based on this fact, one can extrapolate $\langle\alpha\rangle$ and various components of a tensor for every unlimited disubstituted push-pull (D-CNTs-A) single-walled carbon nanotube (5,5).

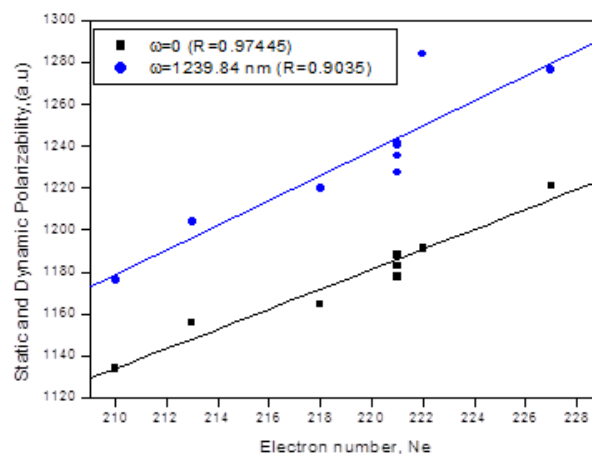


Figure 4: Calculated polarizabilities for substituted CNTs versus the number of electrons.

IV. CONCLUSION

In the present paper, we reported substitutions effects on polarizability for single walled (5,5) armchair carbon nanotubes using semi-empirical PM6 method. It was shown that the strength of Donor/Acceptor groups influences the values of static and dynamic polarizabilities. It also turns out that the pair (NO₂-CNTs-NMe₂) gives the largest values of polarizabilities.

The PM6 semiempirical method yielded an excellent quality of linear correlation for polarizabilities in accordance with empirical models based on molecular volumes, Miller QSAR polarizability and the number of electrons, the correlation coefficient obtained was above 0.97.

The study revealed that the substituted Armchair carbon nanotubes (NO₂-CNTs-D) had large polarizabilities values and hence may have potential applications in the development of nonlinear optical materials (NLO).

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