

Scientific paper

Stabilizing of the Transitory Species $(\text{TiO}_2)_2$ by Encapsulation Into Carbon Nanotubes

Sarrah Dargouthi,^{1,*} Salima Boughdiri² and Bahoueddine Tangour¹¹ University of Tunis El Manar, Research Unity of Modeling in Fundamental Sciences and Diadctics, Team of Theoretical Chemistry and Reactivity, BP 254, El Manar 2, 2096, Tunisia² University of Tunis El Manar, Faculty of Sciences of Tunis, Research Unity of Physical Chemistry of Condensed Materials, El Manar 2, 2096, Tunisia,

* Corresponding author: E-mail: sdargouth@gmail.com

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Abstract

The aim of this paper is studying the encapsulation effect of carbon nanotubes (CNTs) on the stabilizing process of titanium dioxide molecule dimers $(\text{TiO}_2)_2$. First, a theoretical study was performed concerning the guest species that are various titanium dioxide dimers. Five structures were treated as following: i) Cis (C) or ii) Trans (T) relatively to a square shaped fragment Ti_2O_2 , iii) a mixed Tetrahedral/Pyramidal (T/P) disposition while two titanium atoms are sharing three oxygen atoms, and finally not bonded dimers in iv) parallel (P) and v) orthogonal (O) positions respectively. Only the (T), (C) and (T/P) isomers may be considered as stable compounds. The structure of the T-dimer is more stable than the Cis one by only 6.5 kcal mol⁻¹. Typically, intra and extracyclic Ti-O bond lengths are 1.84 Å and 1.61 Å respectively. (T/P) dimer can be described as a metastable structure since its energy is higher than (T) one by 19 kcal mol⁻¹. NBO analysis highlights the participation of dative bonding between oxygen lone pair and vacant titanium 3d orbitals. (P) and (O) structures represent transitory species that transform into the more stable structure which is the T-dimer. The second and principal part of this work concerns the re-optimization of the studied structures placed inside the CNT (12,0). Only (T), (C) and (P) dimers are stabilized by encapsulation through the establishment of strong interactions with the CNT wall. The (T / P) and (O) isomers which are converted into (T) and (P) dimers respectively, are leaving the nanotube while they still interacting with its edge. These favorable results are indicating in one hand the possibly detection of (T) and (C) isomers, and in another hand that the process of polymerization of the TiO_2 molecule which is leading to nanostructured materials could be controlled by encapsulation within the CNTs.

Keywords: Titanium dioxide, carbon nanotube, confinement, encapsulation, transitory species.

1. Introduction

Titanium dioxide is a very interesting and active compound commonly used in industrial processes. TiO_2 mainly exists in crystalline forms such as rutile,¹ anatase² and brookite,³ but it exhibits various morphological shapes on a nanometric scale such as nanoparticles,^{4,5} nanotubes,^{6,7} nanorods,^{8,9} nanowires^{10,11} and nanosheets.^{12,13} Production of nanoparticles of titanium dioxide makes it exhibit new properties that could be applied in many nanotechnological fields. Indeed, given its photocatalytic behavior, TiO_2 is one of the most promising materials for the electrode of DSSCs and is largely used for facilitating the degradation of pesticides in water under the effect of ultraviolet radiations.¹⁴ Added to several other applications that concern sensors, and memory devices.^{15–18}

For all these reasons, the isolated TiO_2 molecule's study has attracted scientists' attention. Unfortunately, it is known that the molecular specie is not easily isolated. It was just possible to characterize it by trapping it in rare gas matrices at very low temperatures.¹⁹ Certain recent works have shown that it is feasible to stabilize intermediate species trapped into carbon nanotubes for relatively short lifetime.^{20–24} We have shown in a recent work²⁵ that it is possible to confine the TiO_2 molecule inside a carbon nanotube (CNT) in a stabilizing way at room temperature. A question then arises, is-it possible to stabilize two molecules of TiO_2 in dimer specie while such entities could be involved as intermediaries in the polymerization process of TiO_2 leading to solid nanostructured compounds?

From the structural point of view, some studies have been explored some TiO_2 polymers.^{26–30} Just like Ti_2O_4 di-

mer, three structures have been investigated and depicted in figure 1. The first, noted (T), exhibits two Ti-O bonds in Trans position relatively to a square shaped Ti_2O_2 motif. The second noted (C), presents a Cis shape relatively to the Ti_2O_2 ring. The third structure, noted (T/P), is based on the formation of a tetrahedron TiO_4 and a trigonal pyramid TiO_3 motifs sharing a planar O_3 triangle. In this paper, we will study the up-mentioned dimers added to two separated TiO_2 molecules in two different positions: parallel, noted (P), and orthogonal, noted (O) respectively.

All the five studied dimers were investigated both inside and outside a carbon nanotube. The used nanotube (12,0), which diameter is 9.401 Å, has been chosen in order to leave weak interaction between tits walls and the two TiO_2 molecules.

2. Materials and Methods

Based on the results of our previous work on the TiO_2 molecule confined in carbon nanotubes,²⁵ all calculations were performed with the DFT/B3LYP technique using the basis set 6-311G (d) which is formed by triple zeta gaussian orbitals including polarization functions. For each dimer, we operated with and without symmetry con-

straints. The two TiO_2 molecules are confined inside the zigzag nanotube (12,0). A restraint optimization with fixed nanotube geometry was imposed in order to keep the quantum calculations in a reasonable consuming time. The C-C bond length was fixed at 1.421 Å. We systematically verified that each optimized structure corresponds to an absolute minimum of the potential energy surface next to the absence of any imaginary frequency. All calculations are done by Gaussian software package.^{31–32}

3. Results and Discussion

Let's begin by recalling few important properties of TiO_2 molecule from our previous work²⁵ which may facilitate further interpretations. Calculated geometry is V-shaped which bond length is 1.640 Å and bond angle is equal to 111.80° (Figure 1). The experimental value is 1.613 Å.¹⁹ The obtained Wiberg index value of Ti-O bond is 1.80 indicating the existence of a double chemical bond. Thus we can normalize it by associating the value of 0.90 for Wiberg index to a single bond Ti-O. The Mulliken electric charges of titanium and oxygen atoms are respectively 0.92 and -0.46 in agreement with the fact that oxygen is more electronegative than titanium. Hence bonds

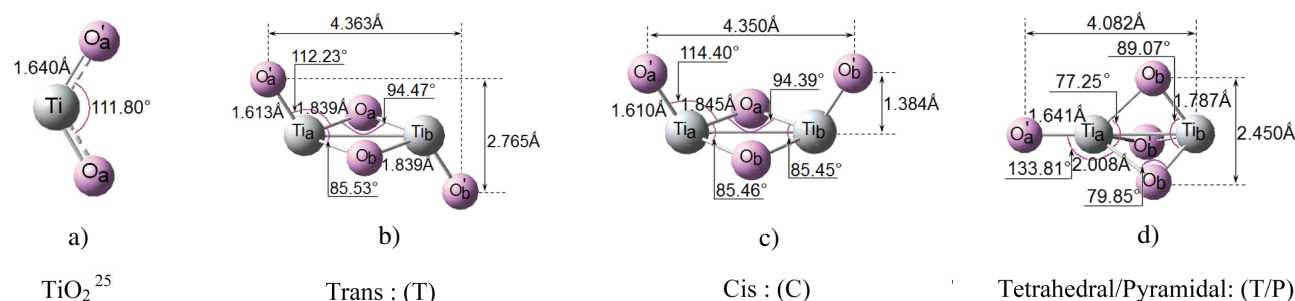


Figure 1. Labeling and selecting geometrical parameters for the studied dimers. TiO_2 molecule is presented for comparison.

Table 1. Energy (in kcal mol⁻¹) and selected geometrical parameters (Bond length in Å and angles in degrees) of TiO_2 dimers. The energy of two separated TiO_2 molecules is considered as reference. Wiberg bond index is indicated in parenthesis.

		(T)- Ti_2O_4 (C_{2h})	(C)- Ti_2O_4 (C_{2v})	(T/P)- Ti_2O_4 (C_1)	TiO_2 ²⁵ (C_{2v})
Energy of stabilization		-81.930	-75.412	-62.930	-
Bond length	Ti_a-O_a'	1.613(1.94)	1.610(1.96)	1.641(1.91)	1.640(1.80)
	Ti_a-O_a	1.839(0.85)	1.845(0.83)	2.008(0.53)	
	Ti_b-O_b	1.839(0.85)	1.845(0.83)	1.787(1.22)	
Bond angle	$O_a'Ti_aO_a$	112.23	114.04	133.81	111.80
	$O_aTi_aO_b$	85.53	85.46	77.25	
	$O_bTi_bO_a$	85.53	85.45	89.07	
	$Ti_aO_aTi_b$	94.47	94.39	79.85	
	$O_a'Ti_aTi_b$	121.02	121.11	179.79	
	$O_aTi_aO_b$				
Dipole moment	μ	0.00	8.98	7.63	6.87
Atomic charge	Ti_a	1.40	1.40	1.49	0.92
	Ti_b	1.40	1.40	1.37	0.92
	O	-0.82	-0.84	-0.77	-0.46
	O'	-0.58	-0.56	-0.58	-0.46

are strongly polarized with a transfer of roughly one electron from titanium to the two oxygen atoms. The dipole moment is equal to 6.87D.

Only the (T), (C) and (T/P) isomers may be considered as stable compounds because they represent absolute minima on their potential energy surfaces. Their stabilization energy calculated by the formula $E = E(\text{Ti}_2\text{O}_4) - 2 \cdot E(\text{TiO}_2)$ is indicated in table 1.

Figure 1 presents studied optimized structures and atom labeling.

As shown in figure 2, Trans dimer is the most stable compound. Results with C_{2h} symmetry and without symmetry constraints are equivalent and both lead to an absolute minimum of the potential surface illustrated by the absence of imaginary frequency. Selected geometric parameters of TiO_2 dimers are gathered in table 1. O' designates an extracyclic position of oxygen. The two optimized Ti-O' bonds in Trans position are 1.613 Å which are a little smaller than 1.640 Å representative of the calculated value of the molecular one. This difference is well supported by Wiberg indexes which are 1.94 and 1.80 respectively. This variation will be interpreted later by the establishment of dative bonds between molecules in each isomer. Moreover, it is plausible to consider that the extracyclic Ti-O' bond is essentially double in nature.

The geometry of the motif Ti_2O_2 is nearly squared plane in shape, the angles 94.47° and 85.53° differ roughly from $\pm 5^\circ$ with respect to the ideal value of 90° . $\text{Ti}_a\text{-Ti}_b$ distance is of 2.700 Å. It is a little larger than the sum of two atomic radius of 1.36 Å indicating the lack of a direct bonding between the two titanium atoms.

The four Ti-O bond lengths of the square are equal to 1.839 Å. This value is larger than the free molecule which bond length is equal to 1.640 Å representing a double bond. Ti-O calculated Wiberg bond index is 0.85 roughly the half of the extracyclic Ti-O' one of 1.94. It can be concluded that all intracyclic Ti-O bonds are almost single in type. Given its symmetry group C_{2h} , this molecule is not polar and its dipole moment is equal to zero.

The second studied compound is the Cis isomer. It is less stable than the Trans one by $6.518 \text{ kcal mol}^{-1}$. This difference is relatively small indicating the possibility of simultaneous existence of these two species at room temperature.

Angles and bond lengths of Cis and Trans isomers are also comparable. We observe a small lengthening of the Ti-Ti distance from 2.700 Å to 2.707 Å and of the intracyclic Ti-O from 1.839 Å to 1.845 Å. Conversely, the extracyclic Ti-O' bond decreased from 1.613 Å to 1.610 Å. Still, these changes are too small to affect the bond orders.

The third dimer is tetrahedral/pyramidal in shape which divides the four oxygen atoms into two groups (3 + 1). Three oxygen atoms are shared between the two titanium atoms while the fourth oxygen remains bounded to only one titanium. Three possibilities can be considered:

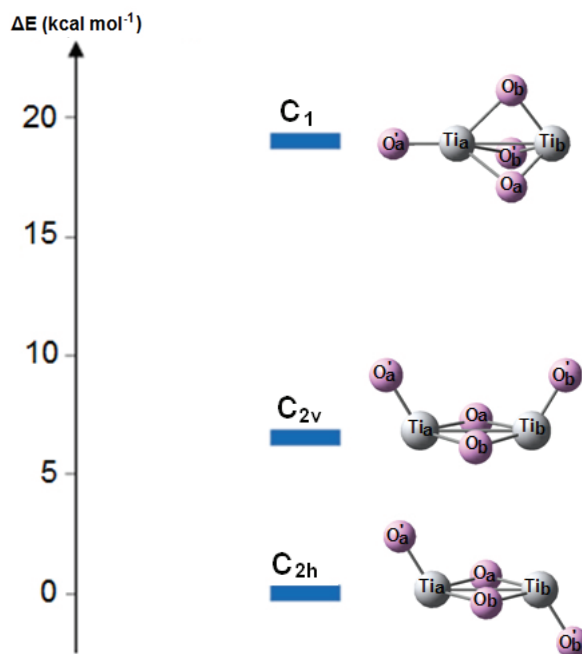


Figure 2. Energy diagram of the studied isomers relatively to the energy of the $\text{T-Ti}_2\text{O}_4$.

C_1 , C_s and C_{3v} symmetries. The obtained optimized structure exhibits zero, one and two imaginary frequencies respectively.

The symmetry cannot be imposed to this dimer and the structure C_1 is the only representative of the physical reality. This isomer is less stable than the Trans one by 19 kcal mol^{-1} . It has a double bond length Ti-O' equal to 1.614 Å and three bonds of variable length between 1.784 Å and 2.015 Å. Their Wiberg indexes are 1.22 and 0.53 largely smaller than 1.80 and 0.9 characterizing double and single bonds respectively. In addition, the angles O-Ti-O are almost equal to 90° with the first titanium atom and equal to 77° with the second one, while the angle Ti-O-Ti is near to 80° . The distance Ti-Ti is 2.441 Å generating a decrease of 9.59 % relatively to the Trans isomer. The (T/P) compound is polar, its dipole moment is 7.212D slightly lower than the Cis shaped one which value is equal to 8.985D.

NBO analyses were performed in order to more understand the nature of the chemical bonds and to interpret their variations. Final proposed Lewis structures are shown in figure 3. NBO analysis indicates that all 3d orbitals of titanium are involved in the establishment of bonds. There are 12 occupied molecular orbitals and only one lone pair in each oxygen atom. Figures 3a and 3d represent the relative approach of the two dimers. For Trans (or Cis) isomers, there are dative bonds from one oxygen lone pair to a titanium 3d vacant orbital (Figure 3b). This donation is responsible of the little Ti-O' bond length shortness indicated above. The dative bonding process is characterized by an energy of $90.62 \text{ kcal mol}^{-1}$ calculated from the

Second Order Perturbation Theory Analysis of Fock Matrix representing an interaction between a bonding Ti-O and an antibonding Ti-O'. By symmetry, all intra-ring bonds are equivalent with a bond order of roughly one.

Because there are three bridged bonds Ti-O in the (T/P) isomer, the two titanium atoms exhibit shorter interatomic distance than (T) or (C) isomers. Moreover, the two oxygen atoms linked to titanium in Ti_b contracts two dative bonds while only one oxygen lone pair of Ti_a is used (Figures 3d–f). So, it is normal that Ti_b -O bond lengths are shorter than the Ti_a -O's ones. Wiberg index of the former is 1.22 corresponding to a bond order of 1.33 as we attribute the normalized value of 0.90 to a single bond. Inversely, Wiberg index of the latter is 0.53 corresponding to a bond order of 0.66.

In all studied dimers, the multitude of titanium-oxygen bonding types has increased dramatically the bond polarization. Titanium exhibits a positive charge of roughly 1.4 in a dimer while the corresponding molecular monomer TiO_2 value is only 0.92. Inversely, the intracyclic oxygen atoms present a very high negative charge of -0.82 but its charge in molecular TiO_2 is only -0.46 . However, the extracyclic oxygen, which kept the double bond character, has a negative charge close to the monomer. It is clear that the increase in polarity is a direct consequence of dative bonding.

Those results highlight the importance of the monomers approach in the process of dimer formation. For this reason, they will be investigated separately. So the fourth studied case concerns two separated molecules in parallel

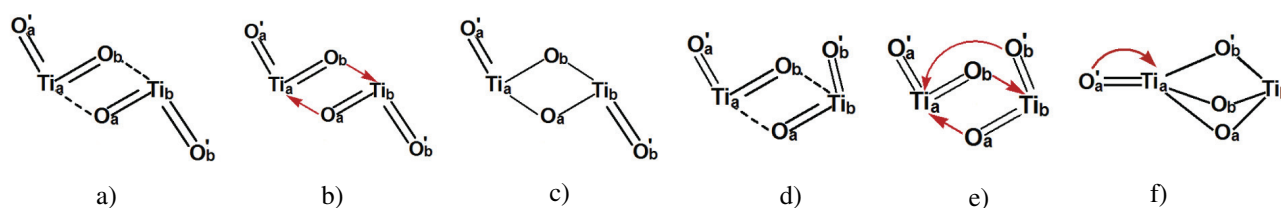


Figure 3. Proposed Lewis structures for studied dimers.

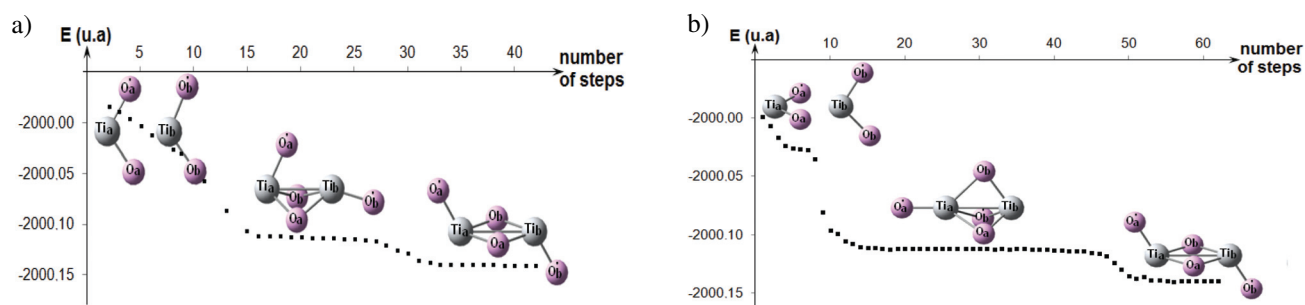


Figure 4. Energetic optimization profiles of separated TiO_2 molecules: a) in parallel and b) orthogonal positions.

Table 2. Confinement energy (kcal mol^{-1}), selected geometrical parameters (Bond length in \AA and angles in degrees) and Mulliken atomic charge of TiO_2 dimers inside carbon nanotube $Ti_2O_4@(12,0)$. Dipole moments are in Debye. Wiberg bond index is indicated in parenthesis.

		(T)@(12,0)	(C)@(12,0)	(O)@(12,0)	$TiO_2@(12,0)$
Confinement energy		-69.436	-77.219	-45.945	-
Bond length	Ti_a-O_a	1.838(0.85)	1.846(0.83)	1.681 (1.54)	1.636(1.80) ²⁵
	Ti_b-O_b	1.838(0.85)	1.846(0.83)	1.672(1.61)	
	$Ti_a-O'_a$	1.622(1.79)	1.619(1.91)	1.680(1.55)	
Bond angle	$O'_a-Ti_a-O_a$	107.30	109.24	98.31	114.567 ²⁵
	$Ti_a-O_a-Ti_b$	94.31	94.07	94.34	
	$O_b-Ti_b-O_a$	85.66	84.61	114.33	
	$O'_a-Ti_a-Ti_b$	113.76	108.08	-	
Dipole moment	M	0.08	0.23	0.49	2.90
	Mulliken charge				
	Ti_a	1.43	1.43	1.44	1.32
	Ti_b	1.43	1.43	1.36	
	O	-0.80	-0.82	-0.70	-0.64
	O'	-0.61	-0.56	-0.79	-0.64

position noted (P). The energetic profile of the optimization (Figure 4a) procedure indicates that those molecules change their direction through the establishment of an interaction between one oxygen atom of one molecule and the titanium atom of another molecule leading to a structure very close to the Tetrahedral/Pyramidal isomer. The most stable isomer, the Trans one, is obtained at the end of the optimization procedure. A comparable behavior (Figure 4b) is observed for the two TiO_2 molecules placed in the orthogonal position noted (O).

The energy optimization profiles (Figure 4) show, for both latter studied (P) and (O) structures, a flat surface section without roughly change in gradient module corresponding to two monomers in interaction occupying orthogonal positions. This does not correspond to a stable structure or to an intermediate reaction with a relative minimum as the (T/P) compound, but it puts in evidence the existence of transitory specie with low lifetime.

Since it is well established that confinement into CNT is able to stabilize low lifetime species,^{15–20} it will be interesting to survey the behavior of the studied species inside carbon nanotubes. We introduced the five structures already studied in the nanotube (12,0) which diameter D is equal to 9.401 Å. Figure 5 depicts the optimized dispositions.

Table 2 displays the confinement energy and few selected geometrical parameters. We note that both Trans and Cis dimers remain confined inside the nanotube and have roughly kept their initial geometry (Figures 5a,b).

This is the consequence of establishing an interaction between the oxygen atoms and the wall of the nanotube as it is shown by the representation of molecular orbitals in figure 6. Nevertheless, the Tetrahedral/Pyramidal compound undergoes a structural change and leaves the CNT. Its final structure is the Trans shaped which corresponds to the most stable isomer (Figure 5c). We can conclude that this (T/P) compound undergoes a metastable situation under the Tetrahedral/Pyramidal shape.

When the two monomers are placed in parallel position inside the nanotube, two separated steps were detected. The two molecules begin to perform a reorientation to the perpendicular position and finish by leaving the nanotube. The final position corresponds to two monomers in perpendicular position interacting with the edge of the nanotube but outside it (Figure 5d).

When the two monomers are placed in orthogonal positions into the nanotube, they maintain their position after optimization (Figure 5e).

The confinement energy is calculated by the following formula:

$$E_c = E [\text{Ti}_2\text{O}_4 @ (12,0)] - E [\text{Ti}_2\text{O}_4] - E [\text{CNT}(12,0)]$$

Interatomic distance Ti-Ti is equal to 2.823 Å while we observe a short lengthening of Ti-O bonds passing from 1.64 Å in monomer to 1.68 Å testifying of the establishment of weak interaction between the two separated molecules.

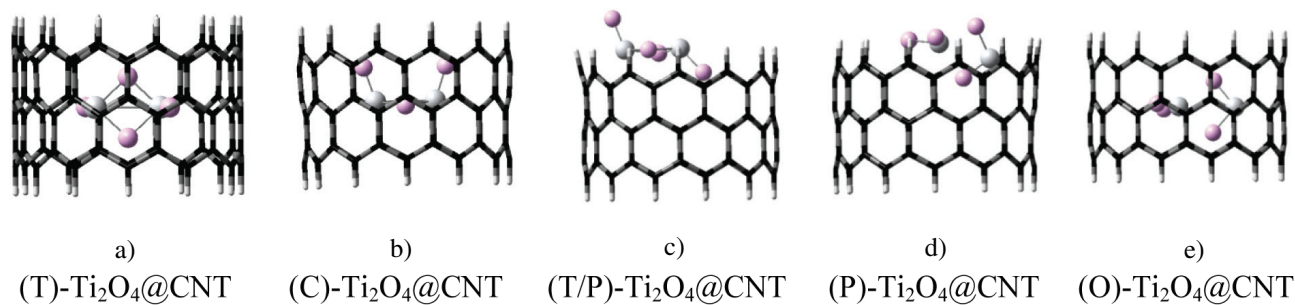


Figure 5. Optimized dispositions of studied dimers into the carbon nanotube (12,0).

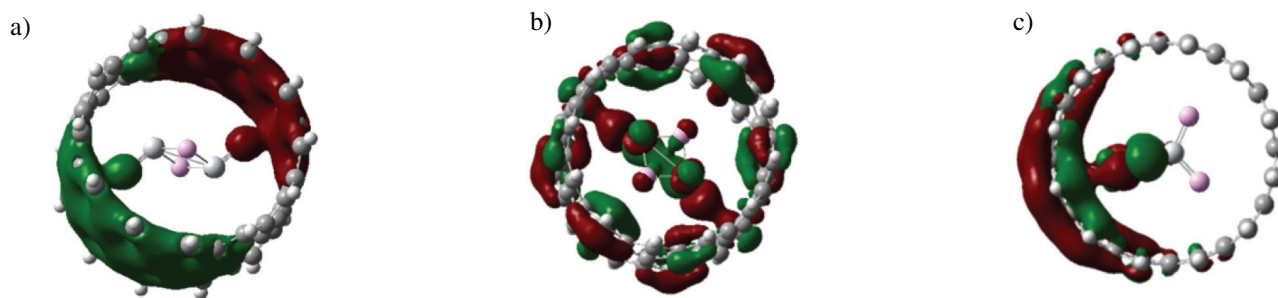


Figure 6. Representations of molecular orbitals for TiO_2 dimers: a) Trans, $E = -0.92013\text{au}$, b) Cis, $E = -0.29406\text{ au}$ and c) Orthogonal, $E = -0.31963\text{au}$. Isoenergetic value is 0.15au.

The stabilization of the (P) dimer by confinement inside the nanotube confirms our previous conclusion about its nature as transient specie. Indeed, it is from this position that the various interactions between monomers lead to three stable structures (T), (C) and (T/P) as it has been proposed in Figure 3.

Confinement into the CNT appears to play a role of decreasing reaction rates which induce a better control of TiO₂ monomer polymerization reactions which are at the origin of the formation of nanostructured compounds as nanoparticles or nanotubes.

4. Conclusion

This work invoked two complementary parts. In the first, we performed a theoretical study of various dimers of molecular titanium dioxide. Five structures were examined. Three among them, the (T), (C) and (T/P) isomers, may be considered as stable compounds because they represent absolute minima on their potential energy surfaces. (T) and (C) may coexist because they are separated only by 6.5 kcal mol⁻¹. But (T/P) dimer is in a metastable state from an energetic point of view. Non bonded dimer (P) transforms into its homologue (O) which has been considered as transitory specie with low lifetime.

In the second part, we highlight the possible stabilization of (T), (C) and (P) dimers by encapsulation inside the carbon nanotube (12,0). This indicates the probable role that plays this transitory specie in the polymerization process of molecular TiO₂. Confinement is suitable to control the fast evolution process and could generate the synthesis of new titanium dioxide nanostructured materials.

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Povzetek

Proučevali smo stabilizacijo dimer titanovega dioksida (TiO_2)₂ s pomočjo enkapsulacije v ogljikove nanoceevke (*carbon nanotubes*, CNTs). Najprej smo izvedli teoretično študijo za različne možnosti dimer titanovega dioksida, v kateri smo obravnavali pet struktur: i) cis (C) ali ii) trans (T) relativno na četverkotnik fragmenta Ti_2O_2 , iii) mešano tetraedrično/piramidalno (T/P) razporeditev, v kateri si dva atoma titana delita tri atome kisika, in končno nevezane dimere v iv) paralelni (P) in v) ortogonalni (O) poziciji. Izkazalo se je, da so stabilne samo (T), (C) in (T/P) izomere, medtem ko (T/P) dimere lahko obravnavamo kot metastabilne. Njihova energija ne namreč za 19 kcal mol⁻¹ višja od energije (T) izomer. Z NBO analizo smo osvetlili možnosti razpoložljivih vezi med kisikovim prostim elektronskim parom in nezasedenimi titanovimi 3d orbitalami. (P) in (O) strukturi predstavljata prehodne speciese, ki se transformirajo v bolj stabilne strukture T-dimer. V nadaljevanju smo se posvetili re-optimizaciji proučevanih struktur, postavljenih v notranjost CNT (12,0). Ugotovili smo, da so z enkapsulacijo stabilizirane samo (T), (C) in (P) dimere zaradi močnih interakcij s stenami CNT. (T/P) in (O) izomere se pretvorijo v (T) in (P) dimere ter zapustijo notranjost nanocevk, a na robu še vedno interagirajo z njimi. Lahko zaključimo, da je z enkapsulacijo v CNTs možno kontrolirati process polimerizacije molekul TiO_2 , ki vodi do nanostrukturiranega materiala.