

# On the conformational disorder of PHTP:oligothiophene inclusion compounds: A semi-empirical and ab initio study

Sergio O. Vásquez \*

*Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Tupper 2069, Santiago, Chile*

---

## Abstract

A study at the semi-empirical and ab initio level of models of the supramolecular architecture of perhydrotriphenylene and terthiophene (PHTP:T3) inclusion compound shows that the observed conformational disorder in this kind of molecular systems is subject to some constraints, the most important is that there exists an important degree of order inside the nanochannels preventing free rotational orientation of the T3 guest molecules as well as free distribution in the axial direction of the channels. For trigonal channels, T3 guests distort in two (planar and non-planar) configurations, depending on size factors of the nanochannels and small changes from the trigonal to orthorhombic symmetry favour the planar configuration of the guest molecule.

*Keywords:* Nanochannels; Perhydrotriphenylene; Inclusion compounds; Oligothiophene; Conformational disorder; Geometry optimization

---

## 1. Introduction

Recently various authors have given attention to inclusion compounds (IC) in matrices formed from perhydrotriphenylene (PHTP) molecules [1–4]. These matrices allow the inclusion and coinclusion of various organic guest species, and they have been studied because of their eventual interest in optoelectronic applications [3,5,6]. The basic crystal architecture of PHTP and a variety of guest molecules correspond to honeycomb type structures made of stacks of perhydrotriphenylene molecules whose layers are about 4.8 Å apart [1,2,7]. These stacks give rise to long one-dimensional cavities or channels that can include the guests when crystallization of PHTP occurs in the presence of those entities. The average crystallographic arrangement is not unique, and it is strongly influenced by factors inherent to the PHTP, as well as the size and shape of the guest molecules. For example, in polar PHTP–IC compounds

such as 1-(4-nitrophenyl)piperazine (NPP) [8,9] the crystals formed are not homogeneous, since it is possible to find monoclinic and orthorhombic regions, as well as regions with pure PHTP. It must also be considered that the perhydrotriphenylene units show chirality: PHTP is a mixture of the *R*-PHTP and *S*-PHTP and the location of each stack is random [2,8]. As to the guest molecules, it has been mentioned that planar molecules give rise to orthorhombic deviations in the unit cell of the IC compound or that non-planar chains would tend to generate some helicity in the channels of the PHTP due to host-guest interactions [8].

Bongiovanni et al. [3,5,7,10] have studied IC compounds with the oligothiophenes terthiophene (T3) and quinquethiophene (T5), both as inclusion compounds, PHTP:T3 and PHTP:T5, and as coinclusion compounds, PHTP:T3,T5, given their particular optical properties and the observation of energy transfer processes between oligomer units. In these systems the separation between the channels makes it possible to obtain systems with high oligomer concentrations, but avoiding the aggregation problems of pure

---

\* Fax: +56 2 699 4119.

*E-mail address:* ovasquez@dqib.uchile.cl

crystalline phases. Experimental evidence indicates that inclusion in PHTP induces planarization of the oligothiophenes, deduced from changes in the electronic spectra. It should be mentioned that planarization is also seen in the solid state and by aggregation in liquids and thin films [11–13].

Experimentally, the real structure of the IC oligothiophenes has not been well resolved, basically because the crystals are not homogeneous and conformational disorder characteristic of such supramolecular architectures. However, initial DRX and absorption and photoluminescence spectroscopy studies by Bongiovanni et al. [7] on PHTP:T5 point to a pseudo-trigonal unit cell with  $a \cong b = 25.3 \text{ \AA}$  and  $c = 43 \text{ \AA}$  ( $9 \times 4.78 \text{ \AA}$ ) and  $\alpha = \beta \approx 90^\circ$  and  $\gamma = 120^\circ$ . The value of  $c$  is accounted for by the inclusion of two molecules of T5 along the nanochannel in the unit cell, corresponding to nine PHTP inter-plane distances and the approximated  $a \cong b$  relation opens the possibility of small orthorhombic symmetry distortions. The relative structural disorder is also reflected in the inner size of the channels, since Bongiovanni et al. only suggest an imprecise inside diameter between  $8 \text{ \AA}$  and  $10 \text{ \AA}$ , although a more precise inter-channel distance of about  $14 \text{ \AA}$  is mentioned [7].

Calculations at the molecular mechanics (MM) level show that the oligomers adopt a non-planar configuration, characterized by S–C–C–S dihedral angles somewhat larger than those in the gas phase ( $147^\circ$ ), but never approaching the planar structure ( $180^\circ$ ). Therefore, even though the planarization effect of included oligothiophenes is known and accepted, these authors' MM results as well as their MINDO quantum calculations [10] do not provide an adequate explanation of this aspect, and the more recent literature does not contribute new information in this respect.

As additional data of IC unit cell size, those deduced by Weber et al. [8] for PHTP:NPP may be mentioned. They correspond to non-homogeneous orthorhombic structures with  $15.054 \text{ \AA} \leq a \leq 15.173 \text{ \AA}$ ;  $23.235 \text{ \AA} \leq b \leq 23.491 \text{ \AA}$ , and  $4.713 \text{ \AA} \leq c \leq 4.779 \text{ \AA}$ , assuming a racemic mixture conformation and pointing to homogeneous homochiral stacks for up to about ten unit cells.

This study carry out a conformational analysis of the PHTP:T3 nanochannel system made from theoretical calculations that provide grounds for a better understanding of the supramolecular architecture and looks at the influence of the interactions between the host and the guest molecules in this IC compound. Ab initio calculations at the RHF/6–311G+(d,p) level of isolated T3 molecules in the ground state and gas phase and also included in models of the channels in PHTP at the semi-empirical PM3 and ab initio RHF/3–21G levels, allow a plausible explanation for the optimum geometry and the degree of planarization undergone by the oligothiophenes in this kind of systems.

## 2. Computational details

Optimization of the geometry of T3 oligomers in the ground state and gas phase was carried out at the restricted

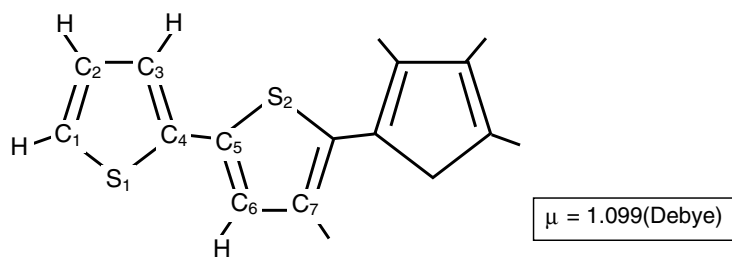
Hartree–Fock level, using the basis set 6-311G + (d,p). The calculation model for PHTP:T3 inclusion compounds considers a simplified structure of 239 atoms with a global composition  $C_{66}H_{170}S_3$ , as explained later. In these entities the oligomers are subjected to a reoptimization of geometry at the semi-empirical PM3 level, although in some cases these results were checked at a an RHF level using the basis set 3–21G, but at a much higher computing cost and achieving results in qualitative agreement to those of PM3.

The calculations were made on an HP Alpha DS25 server, using the Gaussian 03 code [14].

## 3. Results and discussion

The results of geometry optimization for T3 in the gas phase at an RHF/6–311G + (d,p) level of calculation are shown in Fig. 1. Bond lengths and in particular the S–C–C–S dihedral angle of  $147.78^\circ$  are in excellent agreement with the experimental and theoretical calculation data [15,16]. This information was then used to generate a model of the PHTP:T3 inclusion compound. The structure of the PHTP entities was built from the crystallographic data [17], forming the nanochannel with a racemic mixture of alternating *R*-stacks and *S*-stacks and displaced  $c/2$  along the  $c$ -axis, in agreement with the average view proposed by Weber [8]. In order to keep an adequate computational cost, only the innermost layer of the nanochannel was considered, formed by 6 stacks of  $2n$  carbon atoms and  $4n$  hydrogen atoms; where  $n$  is the number of layers that make up each the stack. The carbons were saturated with two additional hydrogens toward the outside of the channel, completing  $6n$  hydrogen atoms in each stack. The channel is modelled as a honeycomb type tubular arrangement of ethane-like molecules, but with the inner carbons and hydrogens respecting and frozen to the positions of the original PHTP structure. In other words, this model assume that the oligothiophene molecules become deformed more easily than PHTP units, in particular by twisting of the S–C–C–S dihedral angles in the oligomers. To account for a reasonable and representative size and symmetry of the channel, the model of the PHTP:T3 entity consider three *R*-stacks made by four layers and three *S*-stacks made by five layers, and the global composition is  $C_{66}H_{170}S_3$ . Trigonal systems were considered as initial reference structures, followed by structures with orthorhombic distortion by compression of side  $b$  of the unit cell, similar to those reported by Weber [8] for the polar compounds PHTP:NPP. Initial optimization of the geometry of the included oligothiophene was made by introducing it with the optimum gas phase geometry into the nanochannel and reoptimizing until convergence. Once founded the patterns of spatial reordering of the T3 oligomer inside the nanochannel, optimizations proceed with this new geometries as initial guesses.

Trigonal nanochannels of different dimensions, typified by their internal diameter as the distance between carbon planes of the honeycomb-like channel, show that the



Bond	S <sub>1</sub> -C <sub>1</sub>	S <sub>2</sub> -C <sub>5</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>	C <sub>3</sub> -C <sub>4</sub>	C <sub>4</sub> -C <sub>5</sub>	C <sub>5</sub> -C <sub>6</sub>	C <sub>6</sub> -C <sub>7</sub>	C <sub>1</sub> -H	C <sub>2</sub> -H	C <sub>6</sub> -H
Length (Å)	1.724	1.737	1.345	1.433	1.352	1.464	1.350	1.430	1.071	1.073	1.074

Fig. 1. Geometrical data and dipole moment for T3 (gas phase/ RHF/6-311G+(d,p) calculation).

geometry of the included T3 changes strongly from the gas phase conformation. As shown in Fig. 2, the geometry varies from non-planar very distorted T3 units in channels of 8 Å to nearly planar configurations in channels of higher internal diameter. The common feature of all these geometries is that the thiophene units are coaxially orientated to the channel and show alignment to the hydrogen rows of the inner wall of the nanochannels, as shown in the frontal views of Fig. 2.

For T3 included in a narrow channels of 8 Å, the minimum of energy found corresponds to oligomers in a non-planar geometry and re-orientating each of the thiophene rings with dissimilar dihedral angles S-C-C-S (about 97° and -160°, respectively), resulting in a very distorted structure as shown in Fig. 2(a). On the other hand, a small increment to 8.5 Å in the diameter channel shows a more planar T3 molecular conformation with dihedral angles of about 162° (see Fig. 2(b)). For channels of 9 Å and bigger, Fig. 2(c) and (d), the dihedral angles increase to nearly planar (from 169° in 9 Å to 175° in 9.5 Å) and there is also the additional chance to obtain molecules of planar geometries with a energy slightly higher than those of the nearly planar conformers (about 0.7 kcal/mol) and then with a big probability to occur. Compare Fig. 2(c) and (f) for a 9 Å channel, where the planar T3 molecule in Fig. 2(f) have dihedral angles of 177°.

Finally, for a wider 10 Å diameter channel, the increment of the internal volume and the reduction of the strength of the interactions between the T3 and the inner wall of the nanochannel leads to a optimum geometry for the guest units that resemble the geometry of the gas phase, with dihedral angles of 146°. However, there is also a higher conformational freedom that results in a variety of non-planar geometries (with dihedral angles ranging from 143° to 169°) at energies lesser than 1 kcal/mol higher than the optimum geometry and showing a partial loosing of the axial alignment.

A plausible explanation of the optimal geometries found for the included terthiophene should arise from the details

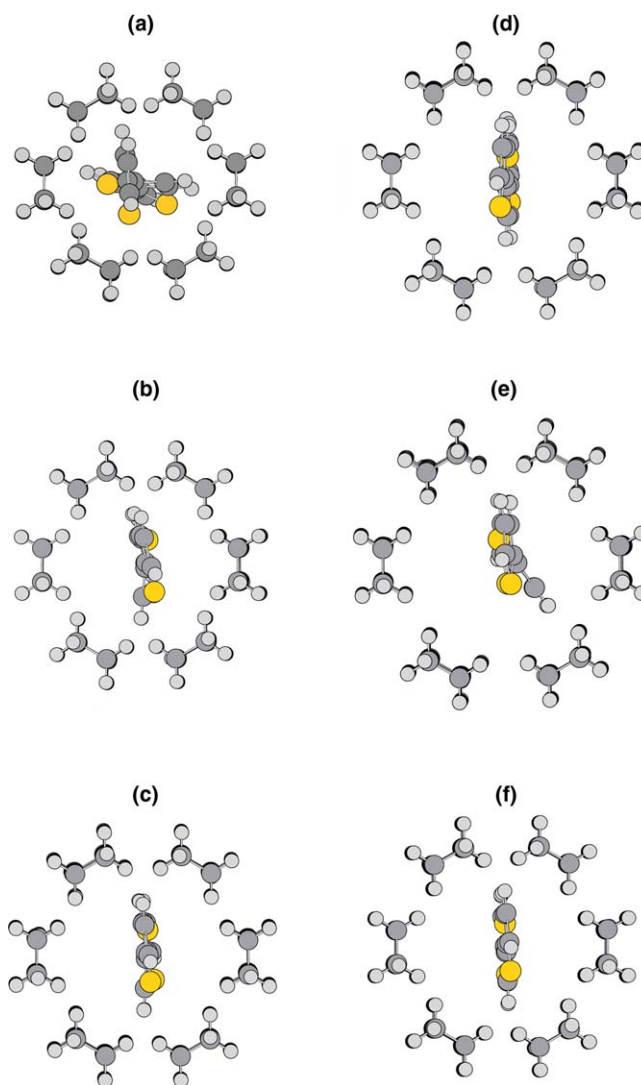


Fig. 2. Frontal view of geometry optimization of T3 for different trigonal PHTP:T3 inclusion nanochannels: (a) 8 Å channel, (b) 8.5 Å channel, (c) 9 Å channel, (d) 9.5 Å channel, (e) 10 Å channel, and (f) T3 in planar geometry included in a 9 Å channel.

of the simultaneous interactions between the electronic clouds near the axially ordered hydrogens of the inner wall of the channel with each of the thiophene rings, via the sulphur atom and the two hydrogen opposite. For narrow channels, a planar geometry for T3 is not allowed by steric reasons and the oligomer suffer a heavy distortion, which is the result of minimizing the highly increased energy of repulsion between the electronic densities of T3 and the closer innermost wall of the channel. In channels of 9 Å and 9.5 Å diameter there is enough internal volume to allow a unfolding of the T3 units, the alignment effect is dominant and always the T3 tend to adopt a geometry closer to planar strongly correlated to the hydrogen atoms of the innermost wall of the channel.

Comparison between the energies of the several optima of geometry as a function of the channel diameter, show that the most favoured conformation is T3 included in a PHTP nanochannels around 9.0 Å, as shown in Fig. 3. This corresponds to a Van der Waals internal diameter of the channels of 6.5 Å, a dimension that is close to the results found by Weber for the wider *a* channel axis of orthorhombic PHTP:NPP [8,9].

As the oligomers always tend to show alignment to the Hydrogen rows of the inner wall, a study on the rotational barrier to free rotations of T3 along the channel axis is carried out, taking the configuration for the optimal geometry as the reference and single point energy calculations of the T3 rotations is shown in Fig. 4(a). Rotational barriers show a regular pattern, with five local minima at  $\pm 60^\circ$ ,  $\pm 120^\circ$  and  $180^\circ$ , relative to the absolute minimum at  $0^\circ$ . It is interesting to note that the three T3 orientations at  $0^\circ$ ,  $+120^\circ$  and  $-120^\circ$  are almost isoenergetic and that are favoured in about 1–2 (kcal/mol) relative to the  $\pm 60^\circ$  and  $180^\circ$ . Rotational barriers are between 4 and 7 (kcal/mol) and the gradient ( $\Delta E/\Delta$  angle) is strong enough to prevent other angular orientations than the six minima. Fig. 4(a) also includes the electric dipole moment data for the system, which changes smoothly and periodically with the rotation of the T3 unit, as a consequence of the change in atomic charges of both the host and the guest molecule. Certainly, consideration of a fixed referential

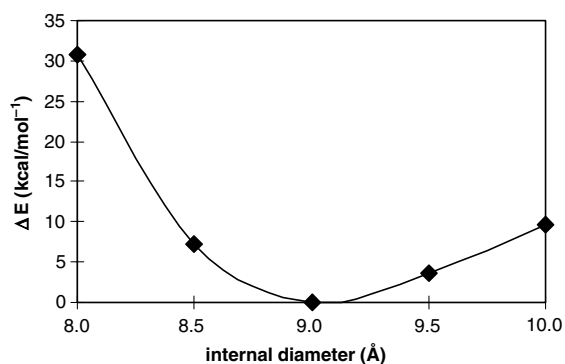


Fig. 3. Optimum conformation of the PHTP:T3 model system as a function of the internal diameter of the nanochannel.

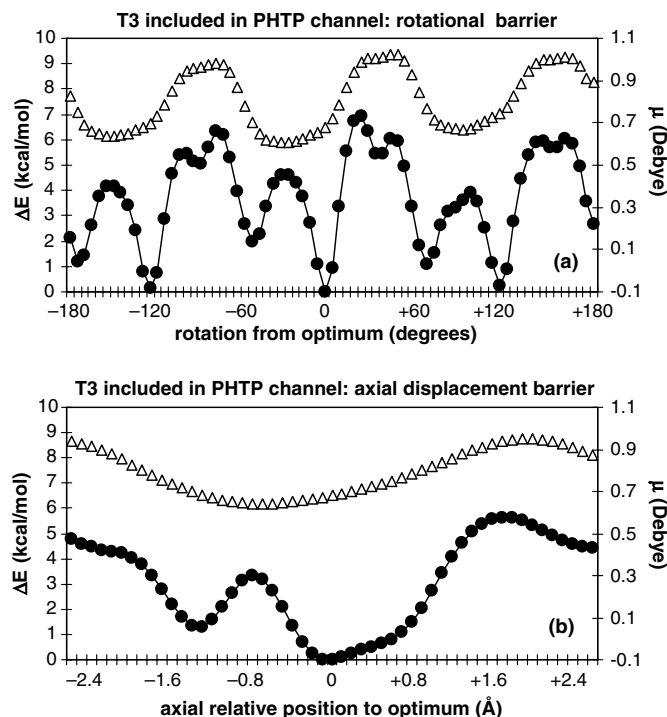


Fig. 4. Energy barriers and change in dipole moment for: (a) rotational and (b) axial displacements of T3 included in a 9 Å trigonal PHTP nanochannels. Displacements are relative to the optimal conformation. Black dots represent energies and triangles dipole moments.

geometry for T3 could be questioned and a relaxation of this assumption is investigated, fixing the central sulphur atom at selected angular orientations and reoptimizing the geometry of the oligomers. Results lead to lower energies but very distorted geometries of the T3 units, a result in conflict to the observed planarization of the oligothiophene units included in the nanochannels and showing that the oligothiophenes are very sensitive to the details of the electrostatic potential surface of the innermost wall of the PHTP channel.

In an earlier study, Bongiovanni et al. [7], showed a frontal view of nearly planar guest molecules orientated in such a way that the T3 plane is located between the two innermost-bonded carbon atoms of two opposite PHTP units. However, examples of optimum geometries drawn in Fig. 2 and the behaviour of the rotational barrier show a different and more reliable configuration where the thiophene ring's plane is nearly coincident with the three-fold plane along the *c*-axis between neighbouring PHTP units. As the molecular orbitals between two adjacent PHTP units do not overlap, these planes do not have any electronic density (i.e., are regions with a nodal character) and allow the coplanar location of a T3 guest molecule with a lower global energy by reduction of the repulsion between electronic clouds.

A second interesting result is that all the optimizations lead to T3 molecules axially aligned in such form that the rings of the T3 remain located in the space between the

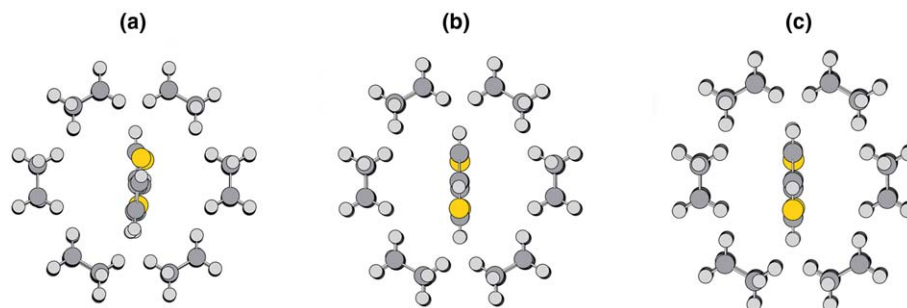


Fig. 5. Changes of the optimal conformation of T3 as the channel distorts from trigonal to orthorhombic: (a)  $a = b$  trigonal symmetry, (b) ( $b/a = 0.95$ ) orthorhombic distortion, and (c) ( $b/a = 0.90$ ) orthorhombic distortion.

PHTP layers. As the width of the thiophene ring is somewhat smaller than the distance between the PHTP layers, the sulphur atom in the central thiophene ring is almost coincident with the mid plane between two PHTP layers of the stack. To investigate this find, single point calculations were made for several conformations, shifting a T3 nearly planar molecule along the  $c$ -axis of a 9 Å nanochannel. The energy of the system shows a periodic behaviour along the channel axis (see Fig. 4(b), with a period coincident to the PHTP inter-plane distance), dictated by the axial location of the layers of  $R$ -stacks and  $S$ -stacks. The maximum translational energy barrier is about 5.5 (kcal/mol) but changes in energy with T3 axial position have a less easier interpretation but dictated by the details on the location of the innermost hydrogen atoms in the  $R$ -stacks and  $S$ -stacks of the PHTP planes. There is also a smooth periodic change in the dipole moment, as the charge densities of T3 change under the effect of the periodic potential induced by the ethane-like structures that conforms the nanochannel. Reoptimization of the T3 geometry fixing the central sulphur atom for different axial positions show a somewhat different result than for rotations: there is a lowering of the energy for the axial barrier but the oligomer geometries found preserve the general planar shape. Changes are small and mostly related to bond lengths and angles between atoms in the thiophene rings.

All these results are indicative that the most significant factor to explain the planar structure of the included oligomers is the great influence of the nodal threefold planes along the  $c$ -axis between PHTP units and that the  $c/2$  separation between PHTP layers of the nanochannel as well as the location of the hydrogen atoms in the innermost wall affect the axial ordering of the guest molecules.

Observation of the calculated 226 molecular orbitals (MOs) show that they can be divided in three crude categories: a massive number of orbitals that belong to the model of the PHTP nanochannel itself; secondly, MOs localized in the guest T3 units at several ranges of energy (for instance, the HOMO is clearly a T3 MO) and thirdly a few MOs that show delocalization between the T3 and the nanochannel and with an interactive character. In general, the MOs have a very small or no contamination between electronic densities of host and guest species,

except for the mentioned delocalized MOs, and preservation of the individual electronic properties is a general result in agreement with the prevalent weak Van der Waals character of the interactions between the host and the guests in this type of supramolecular systems. Molecular orbitals of the model of the channel are very localized into the ethane-like units and show the threefold nodal plane mentioned above. Despite of the crudeness of the channel's model, a more complete structure for the PHTP units should not produce a major change in this characteristic nodal character of the planes between neighbouring PHTP units.

Regarding to the observed few MOs that show interaction between T3 and the PHTP model, a more detailed and careful study is not included here as it requires a very costly calculation at a higher level of theory and with a more complete basis set that is beyond the scope of this work.

A third aspect studied is the effect of distortions of the channel from trigonal to orthorhombic. Fig. 5 shows three geometry optimizations for T3 included in 9 Å nanochannels. As mentioned above, the perfect trigonal case ( $b = a$ ) lead to non-planar T3 molecules with  $169^\circ$  dihedral and nearly planar ( $179^\circ$  dihedral) geometries, being the first slightly favoured for less than 0.7 (kcal/mol). A small orthorhombic distortion ( $b/a = 0.95$ , Fig. 5(b)) induces more easily the planarization of T3 in the plane of longer unit cell dimension (both dihedral angles  $3^\circ$  more planar than the trigonal case) and the energy of the model system lowers in 0.3 (kcal/mol), an effect that is enhanced if the orthorhombic distortion is bigger (see Fig. 5(c)  $b/a = 0.9$ ) where both dihedral angles are  $6^\circ$  more planar than the trigonal case and the energy is 0.4 (kcal/mol) lower. In all the calculations under orthorhombic distortion, the planar oligomers always have the minimum energy and have been found easily due to a convergence faster than for the trigonal case. These results predict planar oligomers as the most common conformation for this slightly distorted conformation.

#### 4. Concluding remarks

Crystallographic information on PHTP inclusion compounds [1,2,8,9] show that they are examples of crystalline



systems with conformational disorder. The 1-D characteristic nanochannels generated by the crystallization of pure PHTP are not homogeneous in size and structure and the eventual inclusion of guest molecules may also produce additional changes in the PHTP host and also in the geometry and localization of the guest. Focusing the study on the molecules included in the host matrix, calculations at the semi-empirical and *ab initio* levels of models of the PHTP:Terthiophene inclusion compound lead to a better understanding of the sources of the observed planarization and the extent of the disorder for the T3 guests inside the nanochannels.

There are three main conclusions in this study: the T3 oligomers tend to distort mostly by twisting of the dihedral S–C–C–S angles, producing conformers that align the thiophene rings planes to the threefold planes that separate the honeycomb-like structure of the PHTP units along the *c*-axis, where the electronic densities are nodal in character. Depending on the channel's internal diameter, the geometry of the guest oligomers may become nearly planar and the source of this effect is the lowering of the repulsion between electronic host and guest clouds in such alignment.

The T3 distortion is a function of the internal diameter of the channels, relaxing from very twisted molecules in narrow channels, due to steric reasons to nearly planar in wider channels. The study also shows that the guest molecules are not randomly distributed inside the channel: barriers to rotational displacements of the guest are important (between 4 and 7 (kcal mol<sup>-1</sup>)) leading to six preferred rotational conformations of T3 (three isoenergetic optima and other three positions about 1 (kcal mol<sup>-1</sup>) higher) coincident with the threefold planes that separate the honeycomb-like structure of the PHTP. There is also some degree of axial guest's order induced by the well-known order of the PHTP units along the *c*-axis.

The conformational disorder of the PHTP host is analysed by the study of the host-guest interaction at different diameter of the nanochannel and also by changing its symmetry from trigonal to orthorhombic. Despite of the simplistic assumptions of the model, results show that the internal diameter of the more stable PHTP:T3 system is in close agreement to the data found in literature and that slight changes to orthorhombic induce easily more planar geometries for T3.

These results improve the understanding of the conformational aspects of this type of systems and could be useful to develop better models of the oligomer–oligomer interaction within the channel architecture, a study that will be published elsewhere [18].

### Acknowledgements

The author acknowledges the financial support of this research from Fondecyt Grant 1030662 and Núcleo Mile-

nio de Mecánica Cuántica Aplicada y Química Computacional Grant P02-004-F.

### References

- [1] M. Farina, G. Di Silvestro, P. Sozzani, in: D.D. McNicol, F. Toda, R. Bishop (Eds.), *Comprehensive Supramolecular Chemistry, Solid-State Supramolecular Chemistry: Crystal Engineering*, vol. 6, Elsevier, Oxford, 1997, pp. 371–398.
- [2] M. Farina, in: J.L. Atwood, J.E.D. Davis, D.D. McNicol (Eds.), *Inclusion Compounds 2*, Academic Press, London, 1984, pp. 69–95.
- [3] C. Botta, R. Bosisio, G. Bongiovanni, A. Mura, R. Tubino, *Synth. Metals* 84 (1997) 535–536.
- [4] G. Bongiovanni, C. Botta, J.E. Communal, F. Cordella, L. Magistrelli, A. Mura, G. Patrinoiu, P. Picouet, G. Di-Silvestro, *Mat. Sci. Eng. C* 23 (2003) 909–912.
- [5] G. Bongiovanni, C. Botta, G. Di Silvestro, M.A. Loi, A. Mura, R. Tubino, *Chem. Phys. Lett.* 345 (2001) 386–394.
- [6] J.C. Sancho-García, J. Bredas, D. Beljonne, J. Cornil, R. Martínez-Alvarez, M. Hanack, L. Poulsen, J. Gierschner, H. Mack, H. Egelhaaf, D. Oelkrug, *J. Phys. Chem. B* 109 (11) (2005) 4872–4880.
- [7] R. Bosisio, C. Botta, A. Colombo, S. Destri, W. Porzio, E. Grilli, R. Tubino, G. Bongiovanni, A. Mura, G. Di Silvestro, *Synth. Met.* 87 (1997) 23–29.
- [8] T. Weber, M.A. Estermann, H. Bürgi, *Acta Cryst. B* 57 (2001) 579–590.
- [9] O. König, H. Burgi, Th. Armbruster, J. Hulliger, Th. Weber, *J. Am. Chem. Soc.* 119 (1997) 10632–10640.
- [10] G. Bongiovanni, C. Botta, J.L. Brédas, J. Cornil, D.R. Ferro, A. Mura, A. Piaggi, R. Tubino, *Chem. Phys. Lett.* 278 (1997) 146–153.
- [11] G. Zhang, Y. Pei, J. Ma, K. Yin, C. Chen, *J. Phys. Chem. B* 108 (2004) 6988–6995.
- [12] N. DiCesare, M. Belletete, M. Leclerc, G. Durocher, *J. Phys. Chem. A* 103 (1999) 803–811.
- [13] F. Meinardi, A. Borghesi, M. Cerminara, A. Sasella, S. Tavazzi, R. Tubino, M. Gurioli, A. Mura, G. Bongiovanni, *Synth. Met.* 121 (2001) 1355–1356.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian03, Revision B.05*, Gaussian, Inc., Pittsburgh PA, 2003.
- [15] N. Di Cesare, M. Belletete, C. Marrano, M. Leclerc, G. Durocher, *J. Phys. Chem. A* 103 (1999) 795–802.
- [16] N. Di Cesare, M. Belletete, C. Marrano, M. Leclerc, G. Durocher, *J. Phys. Chem. A* 102 (1998) 5142–5149.
- [17] D.M. McCann, P.J. Stephens, J.R. Cheeseman, *J. Org. Chem.* 69 (2004) 8709–8717.
- [18] S.O. Vásquez, *Chem. Phys. Lett.* (submitted for publication).